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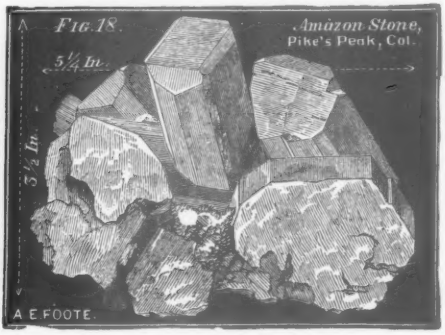

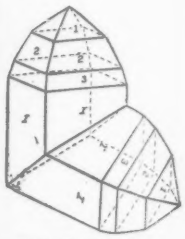

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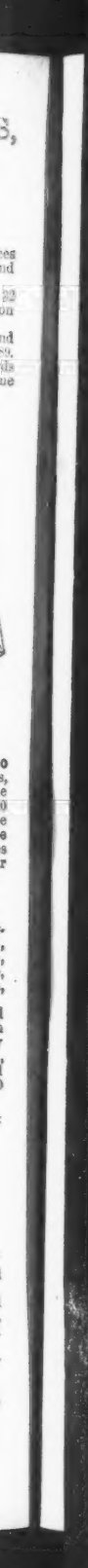


THE

AMERICAN JOURNAL OF SCIENCE

[THIRD SERIES.]

ART. XI.—*The Use of Cupric Nitrate in the Voltameter, and the Electro-Chemical Equivalent of Copper;* by FREDERICK E. BEACH.

[Contributions from the Sloane Physical Laboratory of Yale College.]

AMONG the voltameters in common use the silver voltameter gives results of a very high degree of accuracy, but is not conveniently used except for comparatively small currents. On the other hand the copper voltameter from the cheapness of materials and facility of manipulation finds convenient employment in the laboratory. As ordinarily used with the sulphate of copper, it is subject to certain irregularities due to the attack of the copper by the solution under some conditions, and the oxidation of the metal in others. For these reasons as well as for the fact that excellent deposits of metal are obtained from the nitrate of copper, even with great current densities, it seemed probable that this salt could be successfully used in the voltameter. The object of this paper is to show that cupric nitrate has some marked advantages over the sulphate. For purposes of comparison the results and conclusions of different experimenters will be passed in review.

Gore* expresses the opinion that two independent forces act in the solution, one chemical the other electro-chemical. The action of the former is assisted by a rise of temperature. The loss of the anode is greater than the gain of the cathode, but the chemical corrosion of the anode is less than that of a sepa-

* Nature. March 16, 1882.

rate piece of copper without a current. The purely chemical corrosion of the cathode is more than that of the anode. The addition of any considerable amount of sulphuric acid had the effect of diminishing the weight of copper deposited.

Hammerl* as the result of a detailed investigation comes to the following conclusions:

I. No change in the quantity of the deposit was observed when a blank platinum surface was substituted for one which had been covered with a deposit of copper.

II. The change of concentration of the solution caused by the passage of the current and the polarization dependent on it cannot be satisfactorily prevented by agitation. In boiling to agitate the fluid the deposit oxidizes almost completely to CuO, and partially indeed between 40° and 60° C.

III. The highest allowable current strength is 7 amperes per square decimeter. The distance between the plates should not be less than 1·5^{cm}.

Gray† finds that the highest current-density desirable is one ampere to 50 square centimeters $\left(=0{\cdot}02\ \frac{\text{amp.}}{\text{cm}^2}\right)$. He obtains the ratio $\frac{\text{Cu}}{2\text{Ag}}=0{\cdot}2940$ and for the electro-chemical equivalent of copper 0·0003287 $\frac{\text{gm.}}{\text{amp. sec.}}$ when silver is taken as 0·001118. He remarks "This would indicate a value not differing much from 0·0003290." He does not find as did Gore, that loss by chemical action is less when the current is flowing than when it is not. Copper was dissolved in the sulphate at the rate of 0·02 $\frac{\text{mgm.}}{\text{cm}^2.\ \text{hr.}}$ Addition of sulphuric acid seemed to retard the loss when the density of the solution was between 1·1 and 1·15.

Gray‡ using a density of the sulphate solution of 1·15 to 1·18 with one per cent free sulphuric acid found that the equivalent depended on temperature and current-density in a manner which is exhibited by the following table. The factor 10^{-7} has been omitted.

Area of cathode in sq. cm. per ampere.	Temperature. 2° C.	12° C.	23° C.	28° C.	35° C.
50	3288	3287	3286	3286	3282
100	3288	3284	3283	3281	3274
150	3287	3281	3280	3278	3267
200	3285	3279	3277	3274	3259
250	3283	3278	3275	3268	3252
300	3282	3278	3272	3262	3245

* Wien. Ber., (2), lxxxviii, pp. 273–294. † Phil. Mag., xxii, p. 289, 1886.
‡ Phil. Mag., xxv, p. 179, 1888.

Vanni* found that a solution of copper sulphate of density 1·12 with one per cent of free sulphuric acid dissolved copper, while a solution neutralized with copper hydrate gave an excess. Combining a liter of the normal solution with a half gram of that containing one per cent of the acid neither a gain nor loss could be observed in the weight of a piece of copper immersed in it.

The mean of six experiments with such a solution showed $\frac{Cu}{2Ag} = 0{\cdot}2938$, whence Cu equivalent = 0·0003284 with a current-density between 0·011 and 0·002.

Cintolesi† observed that the solution of a copper plate in copper sulphate depends on the time and the current strength. In vacuo the amount of copper dissolved is less than in air. Oxygen was believed to have an essential influence on the phenomenon.

Shaw‡ using copper sulphate, and a current-density above $0{\cdot}025 \frac{amp.}{cm^2}$ found as a mean of fifteen experiments that the ratio of $\frac{2Ag}{Cu}$ was 3·39983 or Cu equiv. = 0·00032886.

It thus appears that the behavior of copper sulphate had been thoroughly studied; but no quantitative determination had been made with the nitrate, as far as the writer knows, although it had been stated by Smee and others, that the nitrate would bear a much greater current-density than the sulphate.

The apparatus used in the experiments presently to be considered, may be briefly described as follows: the cathode was made from a piece of electrolytic copper about 2^{mm} thick, by bending it so as to form three sides of a rectangle. This was immersed in copper nitrate contained in a glass beaker. The anode was usually a thin sheet of platinum though copper was occasionally substituted for it. The former was much preferred on account of the ease with which the copper is removed by dipping in nitric acid. After rinsing with water the platinum electrode may be dried by heating to redness in a Bunsen flame. The current was measured by the silver voltameter when small, and a Thomson Balance in a few instances when the total current was large. The value of the equivalent of silver used in calculating the numbers hereafter given was 0·0011181, the mean of the value 0·0011183 found by Kohlrausch§ and 0·00111794 the one given by Rayleigh.‖

* Wied. Annal., x, p. 214, 1891.
† Beiblätter, xvi, p. 80, 1892.
‡ Phil. Mag., xxiii, p. 138, 1887.
§ Wied. Annal., xxvii, p. 57, 1886.
‖ Phil. Trans., p. 439, 1884.

It was found early in the course of the work that when the nitrate solution was freshly prepared, it had a tendency to dissolve copper, and that this tendency which was due to the solvent action of the solution itself or the presence of a small quantity of free acid, decreased after the copper electrode had been kept in the solution a sufficient length of time, and that this latter effect seemed to be facilitated by the passage of the current. On the other hand another difficulty to be contended with was the oxidation of the copper deposited after the solution had been used too many times or the current was pushed too far, causing in many cases a darkening or even perceptible blackening of the metal. It was however discovered that the blackening due to oxidation could be prevented by the addition of a small amount of ammonium chloride.

Experiments were now made in which the current density was varied through a considerable range with results which are given in the following table:

No.	Solution.	Current-Density amperes. cm^2	Cu. Eq. $\times 10^7$
1	$Cu2NO_3$ nearly neutral without NH_4Cl,	0·035	3291
2	" "	0·065	3291
3	" "	0·144	3293
4	" "	0·024	3293
5	" "	0·83	3305
6	$Cu2NO_3$ with NH_4Cl,	0·114	3290
7	"	0·074	3297
8	"	0·076	3298
9	"	0·094	3299
10	"	0·019	3290
11	"	0·048	3297

These values show no dependence on the current-density except No. 5 where the large value of the equivalent is best accounted for by oxidation caused by the excessive current. This deposit was badly fringed at the edge and easily detached. Numbers 1–5, made by repeated use of the same solution, show more uniformity than was at any other time obtained from a solution without ammonium chloride present. Attention may be called to what appears to be evidence of the neutralization of the solvent effect of the nitrate on the copper in the gradual but not always regular increase in the values obtained from the same solution in successive experiments.

Having now obtained a fair control of both the tendency to oxidation and solution, experiments were next undertaken with a view to determining the value of the electro-chemical equivalent. With the exception of Nos. 1–5 already quoted, the

solutions used in obtaining the numbers given in the 1st Series were alike in that they were neutral with respect to the copper and contained NH_4Cl.

First Series.		Second Series.	
No.	Equivalent × 10^7	No.	Equivalent × 10^7
1	3291	33	3294
2	3291	34	3296
3	3293	35	3290
4	3293	36	3293
5	[3305]	37	3295
12	3296	38	3294
13	3297	39	3296
14	[3305]	40	3298
15	3293	41	3293
16	3294	42	3291
17	3296	43	3292
18	3294	44	3302
19	3292	45	3296
20	3300	46	3293
21	3299	47	3294
22	3299	48	3291
23	3291	49	3292
24	3295	50	3293
25	3294	51	3292
26	3292	52	3293
27	3300	53	3292
28	3292	54	3291
29	3296	55	3298
30	3301		
31	3291		
32	3295		

The mean of the First Series, including Nos. 5 and 14, is $3295{\cdot}6 \pm 0{\cdot}54$. If these experiments be excluded we get $3294{\cdot}8 \pm 0{\cdot}43$.

Neutralization of the solution in the experiments described had been effected by repeated use. A readier method which suggested itself was to boil the nitrate in order to expel the air, allowing a piece of clean copper to stand in the hot solution until its solvent action had been exhausted. Such solutions were prepared and after the addition of a small amount of NH_4Cl yielded values tabulated in the Second Series, the mean of which is $3293{\cdot}9 \pm 0{\cdot}4$.

In some cases the solutions employed were used many times so that the tests to which the nitrate has been subjected are in this respect particularly severe. There is good reason for supposing that the numbers would have been more consistent if a fresh solution had been used each time.

It is natural to inquire how the values found agree with the equivalent calculated from the atomic weight of copper.

The last named quantity has been investigated with great care by T. W. Richards* with the following result:

If silver be taken as 108·00, oxygen as 16·000 and bromine 80·007

From	Cu : 2Ag	he finds	Cu = 63·640
	Cu : (2AgBr)		Cu = 63·648
	$CuBr_2$: 2Ag		Cu = 63·643
			Cu = 63·644

whence we get

$$\frac{Cu}{2Ag} = 0{\cdot}29465$$

and Cu Equivalent = 0·00032944
when silver is taken = 0·0011181

Hence the value here found is substantially in accord with Richards'. In making this comparison it must be borne in mind that the present investigation was not undertaken for the purpose of finding the equivalent of copper but to determine how well the nitrate would serve as the electrolyte in the copper voltameter and that too, throughout a considerable range of conditions. That these conditions when working with such a sensitive metal as copper were sometimes unfavorable to uniformity of result may be sufficient to explain the amount of variation from the mean. The probable error of a single observation in the Second Series is ± 1·9.

Further experiments were tried to determine the effect of variations in the temperature. Here again it is to be remembered that the solutions were not freshly prepared. A considerable change of temperature either up or down seemed to favor oxidation, but more particularly the latter, probably on account of the increase in concentration of the salt when cooled. Still even this was in great measure prevented by a sufficient addition of the ammonium chloride.

No.	Solution.	Temperature.	Equivalent × 10^7.
56	$Cu2NO_3$ with NH_4Cl	19°	3296
57	Same	6	3297
58	Same	34	3292
59	Same	29	3321
60	Another solution	18	3291
61	Same	36	3297
62	Same	37	3296
63	Same	6	3313
64	Same	10	3307
65	A different solution	40	3291
66	Same	10	3292

* Proc. Amer. Acad., xxiii, p. 177. Ibid, xxv, p. 212.

From these experiments we may conclude that a moderate change of temperature is not a critical matter.

The First and Second Series were made at the temperature of the room which did not vary much from 19° C.

The following method is recommended for the preparation of the solution: Dissolve copper nitrate, the purest obtainable, in distilled water. Boil for a short time to expel the air and keep at a temperature of 100° C. for an hour or two in the presence of bright metallic copper in order to completely neutralize the solution. When ready for use it should have a density of about 1·53. Add a saturated solution of NH_4Cl at about the rate of 1 drop to 100^{cc} of the nitrate. Just the proper amount of ammonium chloride it is not easy to specify. If too much be present the deposit will discolor on drying; if too little, bubbles will collect on the cathode or the deposit will oxidize in the solution. Perhaps the surest way is to try a preliminary experiment, adding the NH_4Cl till the plate begins to show discoloration on drying.

If the solution is to stand the anode may be left in it. Care should be taken to exclude the air.

On removal from the solution the cathode should be washed thoroughly in running water and drained until it may no longer be said to be wet, after which gentle heat should be cautiously applied until all moisture is removed.

The advantages possessed by the nitrate may be enumerated as follows:

1st. The weight of copper deposited does not appear to depend on the current density.

2d. It permits the use of a high current-density.

The limit is not easily stated. When 0·25 amperes per square centimeter is reached the cathode needs watching, for it will fringe at the edge but does not become powdery.

No way was found to prevent the branching with a high current-density.

A greater amount of NH_4Cl should be present when the current density is increased.

3d. The weight of copper is practically independent of the temperature between 10° and 35° C.

The tendency to oxidation is increased by lowering the temperature but this may be easily counteracted by the addition of more NH_4Cl.

4th. The solution may be used a number of times.

5th. The equivalent agrees to four figures with that calculated from the best chemical determinations, viz:

Richards	Eq.	$=(3294{\cdot}4 \pm 0{\cdot}1) \times 10^{-7}$
First Series	Eq.	$=(3294{\cdot}8 \pm 0{\cdot}43) \times 10^{-7}$
Second Series	Eq.	$=(3293{\cdot}9 \pm 0{\cdot}39) \times 10^{-7}$

The purity of the nitrate as a condition of success is to be emphasized. One specimen tried, which contained nitrite, was absolutely worthless with the foregoing treatment.

To see what $CuSO_4$ would do under circumstances similar to those in which the nitrate was studied, a saturated solution of the sulphate was rendered neutral by the copper hydrate precipitated on addition of ammonia. NH_4Cl was added until the deposit was as bright and lustrous as that formed in an acid sulphate solution.

Three such experiments yielded

$$\text{Eq.} = 3295 \times 10^{-7}$$
$$\text{Eq.} = 3293 \times 10^{-7}$$
$$\text{Eq.} = 3294 \times 10^{-7}$$

Two other experiments in circuit with the nitrate showed

	Sulphate. gms.	Nitrate. gms.
Copper deposited	0·4722	0·4719
do. do.	0·5671	0·5667

These values tend to confirm the result obtained from the nitrate; at least they do not contradict it.

In conclusion I wish to express my thanks to Professor A. W. Wright, under whose direction the preceding investigation was made, for his many kind and helpful suggestions.

Sloane Physical Laboratory, June 1st, 1893.

ART. XII.—*On the Double Halides of Arsenic with Cæsium and Rubidium; and on some Compounds of Arsenious Oxide with the Halides of Cæsium, Rubidium and Potassium;* by H. L. WHEELER.

No compounds of arsenious halides, with alkaline halides, have been definitely described. Nicklès* in his work on the bromides and iodides of arsenic, antimony and bismuth, states that these salts combine with alkaline bromides and iodides respectively, but in the case of arsenic he gives no analyses of the compounds which he obtained and he does not describe the methods that he used in preparing them. He does not even state with what alkaline halides he performed his experiments. Emmet†, Harms‡, Schiff and Sestini§ have described

* Compt. Rend., xlviii, 839; Journ. Pharm., III, xli, 142; Rép. chim. pure, i, 366.

† This Journal, I, xviii, 58.

‡ Ann. Chem. Pharm., xci, 371.

§ Ibid., 228, 72.

compounds of arsenious oxide with potassium halides, but this class of bodies has been most thoroughly studied by Rüdorff.* His results indicate the existence of two types of this class of compounds, the first containing one molecule of alkaline halide to one of arsenious oxide, the other having these constituents in the ratio 1 : 2. In the present investigation a complete series of the cæsium and rubidium oxyhalides of the 1 : 1 type was obtained, while the formation of the 1 : 2 type was not observed. There is evidently a gradation in stability from the oxychlorides to the oxyiodides, the stability increasing with increasing atomic weight of the halogens. Attempts to prepare double halides of pentavalent arsenic were without success.

The new compounds to be described in this article are the following :

$3CsCl.2AsCl_3$	$3CsBr.2AsBr_3$	$3CsI.2AsI_3$
$3RbCl.2AsCl_3$	$3RbBr.2AsBr_3$	$3RbI.2AsI_3$
$CsCl.As_2O_3$	$CsBr.As_2O_3$	$CsI.As_2O_3$
$RbCl.As_2O_3$	$RbBr.As_2O_3$	$RbI.As_2O_3$

The compound $As_2O_3.KI$ which had not been observed by Rüdorff† was obtained in attempts to prepare a double iodide of potassium and arsenic.

It is to be noticed that only one type of double halides was obtained. This type corresponds to the most readily prepared double chloride of cæsium with antimony, described by Remsen and Saunders‡ and of cæsium and bismuth, described by Remsen and Brigham.§ Many attempts were made to prepare arsenic double halides of other types than this single one, but these have invariably been without success, although several types of antimony and bismuth double halides have been described.

It has been shown in several instances by Wells and Wheeler‖ that cæsium and rubidium halides form more stable or more complete series of double salts than the halides of the other alkali-metals. This fact is again well illustrated in the double halides of arsenic, for the cæsium and rubidium double halides are prepared without difficulty, while with potassium no double halides were obtained.

Methods of preparation.—To prepare the double halides, a strong acid solution is necessary, in order to prevent the decomposition of the arsenious halide and the consequent formation of oxy-compounds. The double halides are less

* Ber. d. Deutsch. Chem. Ges., xix. 2668; ibid., xxi, 3053.
† Loc. cit.
‡ Am. Chem. Jour., xiv, 152.
§ Ibid., p. 161.
‖ This Journal, III, xlii. 475; III, xliv, 42.

soluble in the strong than in the dilute halogen acids. Excess of one or the other of the constituents has no effect on the composition of the products obtained. The formation of As_2O_3 compounds was observed on treating the double halides or a solution of the constituents in strong acids, with water or dilute acids. The oxygen compounds are difficultly soluble in dilute acids, strong acids convert the cæsium and rubidium compounds into the double halides.

Method of Analysis.

The salts were filtered on the pump and without delay were carefully freed from the mother liquor by pressing on paper. They were then dried in the air. In no case was water used to wash them. In order to determine arsenic the salt was dissolved in the cold in HCl sp. gr. 1·1 and hydrogen sulphide passed in for about one hour; then a little alcohol was added, the whole was warmed on the water bath for a short time, in order to drive off the excess of hydrogen sulphide and effect the separation of the last traces of arsenious sulphide. The sulphide of arsenic was collected on a Gooch filter and after washing with water, alcohol and carbon disulphide it was dried at 100° and weighed. Sulphuric acid was added to the filtrate and the alkali-metal determined as normal sulphate by evaporating and igniting the residue in a stream of air containing ammonia. The halogens were determined in a separate portion as silver halides in the usual manner.

The Double Halides.

Cæsium and Rubidium Arsenious Chlorides: $3CsCl.2AsCl_3$ and $3RbCl.2AsCl_3$.—These have a pale yellow color like the corresponding antimony and bismuth double chlorides. The cæsium salt was obtained by dissolving 250 gms. of CsCl in dilute HCl. 2 grams of As_2O_3, in dilute HCl were then added. This produced a precipitate which dissolved on the addition of about 2 liters of hot HCl sp. gr. 1·1. On cooling, light yellow crystals were deposited. A portion of these was recrystallized from a strong HCl solution of $AsCl_3$. The rubidium salt was prepared in the same manner, except that much stronger solutions were required. Saturated solutions of rubidium and arsenic chlorides in 20 per cent HCl produce no precipitate on mixing but if concentrated HCl is added, brilliant spangles of the double salt separate. The analysis of these products gave :

	Prepared with excess of CsCl		Prepared with excess $AsCl_3$	Calculated for $3CsCl.2AsCl_3$
Cs	46·14	45·27	45·09	45·04
As	17·15		17·11	17·27
Cl	36·89	36·74	36·12	36·79

	Found.	Calculated for $3RbCl2AsCl_3$
Rb	35·55	35·33
As	20·14	20·66
Cl	44·04	44·01

Both salts can be recrystallized from hydrochloric acid of sp. gr. 1·1. 100 parts of HCl sp. gr. 1·2 dissolve ·429 parts of the cæsium salt and 2·935 parts of the rubidium compound. Since the corresponding potassium salt apparently does not exist, these solubilities suggest a convenient method for obtaining cæsium and rubidium free from potassium.

Cæsium and Rubidium Arsenious Bromides: $3CsBr.2AsBr_3$ and $3RbBr.2AsBr_3$.—These are amber-yellow, the shade being somewhat darker than that of the chlorides. They are most conveniently prepared by using an excess of the alkaline halide. Strong hot solutions of the alkaline bromides were made in about 40 per cent HBr. On adding crystals of $AsBr_3$ these melted but soon solidified to a yellow mass of the double halide. This dissolved on boiling, and, on cooling, brilliant yellow crystals were obtained. These compounds can be recrystallized unaltered from strong HBr. Analysis gave:

	Found.	Calculated for $3CsBr.2AsBr_3$
Cs	31·91	31·44
As	11·89	11·82
Br	56·94	56·74

	Prepared with excess of RbBr	Prepared with excess of $AsBr_3$	Calculated for $3RbBr.2AsBr_3$
Rb	23·35		22·77
As	12·55		13·31
Br	63·97	64·43	63·92

Cæsium and Rubidium Arsenious Iodides: $3CsI.2AsI_3$ and $3RbI.2AsI_3$.—These are deep red, the larger crystals of the cæsium compound are more opaque and appear black. To prepare these compounds the normal alkaline iodides were dissolved in strong colorless hydriodic acid and these solutions were then saturated boiling with crystals of AsI_3. Unless the hydriodic acid is decolorized the product obtained in the case of the cæsium salt is generally impure, being mixed with CsI_3.*

* This Journal, xliii, 17; Zeitschr. f. Anorg. chem., i, 85.

A well crystallized product of the double cæsium salt was obtained by preparing the salt in the presence of considerable alcohol. Analysis of these compounds gave

		Calc. for $3CsI.2AsI_3$			Calc. for $3RbI.2AsI_3$
Cs	24·38	23·58	Rb	16·86	16·55
As	8·92	8·87	As	9·96 10·60	9·68
I	67·23	67·55	I	73·65	73·77

An attempt was made to prepare potassium arsenious chloride by mixing solutions of potassium chloride and arsenious acid, saturated solutions of these substances in concentrated HCl being used for the purpose. No precipitate was thus produced, and, on concentrating the solution, potassium chloride was deposited. Aqueous solutions of potassium chloride, when added to solutions of arsenic trioxide in concentrated HCl, gave precipitates consisting chiefly of As_2O_3. Analogous experiments with potassium bromide and arsenious bromide gave similar results, and operating in the same way with KI and AsI_3 in concentrated HI solutions, nothing but crystals of AsI_3 or mixed crops of AsI_3 and KI were obtained. Similar negative results, in respect to the formation of double halides of ammonium and arsenic, have been obtained by Wallace.†

Compounds of Arsenic Trioxide with Alkaline Halides, $CsCl.As_2O_3$ and $RbCl.As_2O_3$:—When a hot saturated aqueous solution of 25 grams of cæsium chloride was saturated with $3CsCl.2AsCl_3$, a finely divided white precipitate was formed on cooling, (Analysis 1.) When 6·5 grams of the double chloride were dissolved in 800cc of a cold-saturated solution of As_2O_3 in HCl of sp. gr. 1·1 by the aid of heat, a similar precipitate was obtained (analysis 2). Products intermediate in composition were obtained by recrystallizing the double halide from water (analysis 3), from 10 per cent HCl (analysis 4) and from 15 per cent HCl (analysis 5).

	1.				2.	3.
Cs	41·51	41·85	41·75	41·80	25·56	34·29
As	35·59	34·58	35·37		47·64	43·05
Cl	11·46		11·31		11·64	8·86
O	[11·44]		[11·57]		[15·16]	[13·80]

	4.	5.	Calculated for $CsCl.As_2O_3$
Cs	35·30	33·92	36·29
As	39·14	38·10	40·93
Cl	10·63	11·42	9·68
O	[14·93]	[16·56]	13·10

† Phil. Mag. IV, xvi, 358; xvii, 122, 261.

The analyses show a considerable variation from the composition required by the formula, the products made under the extreme conditions giving ratios of arsenious oxide to cæsium chloride of 3 : 4 and 3 : 2 instead of 1 : 1. The conditions varied so widely however that it seems fair to assume the existence of a 1 : 1 compound.

When the double chloride of rubidium was recrystallized from about 15 per cent HCl, a white crystalline crust was obtained on slowly cooling. This gave analytical results agreeing with the formula $RbCl . As_2O_3$.

		Calculated for $RbCl . As_2O_3$
Rb	26·90	26·80
As		47·03
Cl	11·41	11·13
O		15·04

Under the microscope these compounds appear as irregular grains or plates, of indefinite crystalline form.

$CsBr . As_2O_3$ and $RbBr . As_2O_3$.—When the double bromides are recrystallized from water, or dilute HBr, they yield these oxy-compounds, and these generally separate in the form of a white crust on the bottom and sides of the beaker. Analysis of such products gave:

	$3CsBr . 2AsBr_3$ recrystallized from water.	$3CsBr . 2AsBr_3$ recrystallized from CsBr solution.	Calculated for $CsBr . As_2O_3$
Cs	32·42		32·36
As	36·52		36·50
Br	19·57	19·59	19·46
O	[11·49]		11·68

	$3RbBr . 2AsBr_3$ from dilute HBr.	$3RbBr . 2AsBr_3$ from water.	Calculated for $RbBr . As_2O_3$
Rb	24·24	16·56	23·52
As	40·06	50·74	41·27
Br	24·53	15·91	22·01
O	[11·17]	[16·79]	13·20

It is to be noticed that the product obtained by recrystallizing $3RbBr . 2AsBr_3$ from water is impure, while the cæsium compound made in the same way corresponds to the formula. This is an illustration of the greater tendency of the cæsium halide to form double salts than in the case of the rubidium halide. Both these compounds are white, but the rubidium compound turns somewhat yellow on drying. Under the microscope, six sided plates were seen in the case of the cæsium compound when the solution was slowly cooled. There were also observed hexagonal crystals with a short columnar rhombohedral habit. They were uniaxial with weak, negative

double refraction. The rubidium compound was also obtained in hexagonal crystals showing rhombohedral symmetry and weak negative double refraction.

CsI. As_2O_3, RbI. As_2O_3 and KI. As_2O_3.—The formation of these compounds was observed when dilute hydriodic acid solutions of the alkaline iodides were mixed with dilute acid solutions of AsI_3. If the solutions are mixed while hot these double salts separated on cooling in the form of crystalline yellow crusts on the bottom and sides of the beaker. These crystals are generally somewhat larger than those of the compounds of As_2O_3 with the chlorides and bromides. Under the microscope they exhibited the form of six sided plates. These show a strong negative double refraction.

The potassium compound also appeared in the form of six sided plates; these remained dark when rotated between crossed nicols. They were too small to afford an axial figure as the largest plates did not exceed 0·01^{mm} in diameter. They are probably hexagonal. Analysis gave:

		Calculated for $CsI . As_2O_3$
Cs	29·31	29·04
As	32·01	32·75
I	28·94	27·73
O	[9·74]	10·48
		Calculated for $RbI . As_2O_3$
Rb	20·35	20·83
As	36·78	36·54
I	31·94	30·93
O	[10·93]	11·70
		Calculated for $KI . As_2O_3$
K	10·75	10·74
As	42·85	41·20
I	34·13	34·88
O	[12·27]	13·18

Crystallography.

The crystallization of the cæsium and rubidium arsenious halides is hexagonal. They were all measured and found to be isomorphous. In general the habit was holohedral, although in the case of cæsium arsenious bromide it is rhombohedral. All these salts show a pronounced basal cleavage, and plates parallel to this, examined with the stauroscope, are uniaxial: the double chlorides and bromides show a weak negative double refraction while the double iodides are positive. The forms observed are as follows:

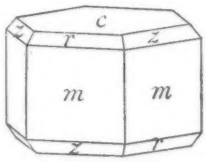
c	0001	*O*	*r*	$10\bar{1}1$	1
a	$11\bar{2}0$	*i*-2	*z*	$01\bar{1}1$	—1
m	$10\bar{1}0$	*I*	*p*	$20\bar{2}1$	2

The steep pyramid *p* was found only on the iodides.
The following table gives the lengths of the vertical axes.

	a	:	*c*
$3CsCl.2AsCl_3$	1		1·209
$3RbCl.2AsCl_3$	1		1·210
$3CsBr.2AsBr_3$	1		1·219
$3RbBr.2AsBr_3$	1		1·220
$3CsI.2AsIs_3$	1		1·244
$3RbI.2AsI_3$	1		1·243

A comparison of the above axial ratios shows the interesting fact that the substitution of rubidium for cæsium produces no appreciable effect in the lengths of the axes, and that in this series the vertical axes lengthen as the atomic weight of the halogens increases. The crystals were sufficiently stable to yield good measurements, although on long exposure they usually lose their luster. In the lists of measurements the angles chosen as fundamental are noted by an asterisk.

1.

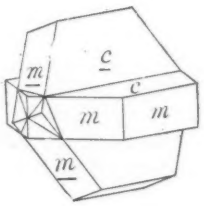


$3CsCl.2AsCl_3$.—This salt was made in crystals about 1–2^{mm} in diameter. The forms observed are *m*, *a*, *r*, *z* and *c*. A careful search was made for indications of a rhombohedral development of the faces *r* and *z*, but none was found. Apparently they are always holohedral in their development, fig. 1.

		Measured.	Calculated.
$m \wedge c$	$10\bar{1}0 \wedge 0001$	90°	90°
$c \wedge r$	$0001 \wedge 10\bar{1}1$	*54 24′	
$r \wedge m$	$10\bar{1}1 \wedge 10.0$	35 39	35 36′
$m \wedge z$	$10\bar{1}0 \wedge 01\bar{1}1$	66 3	66 1
$r \wedge z$	$10\bar{1}1 \wedge 01\bar{1}1$	47 53	47 58

There is a rather poor prismatic cleavage and plates parallel to this show parallel extinction.

2.



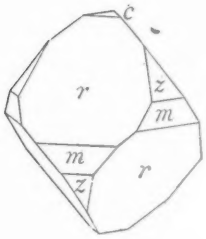
$3RbCl.2AsCl_3$.—This salt was made in crystals up to about 5^{mm} in diameter. The forms observed are *c*, *m*, *r* and *z*. The faces *r* and *z* were seldom present, but when these did occur it could not be seen whether they exhibited rhombohedral symmetry or not. Penetration twins are common, the twinning plane being the rhombohedron $0\bar{1}11$, fig. 2.

		Measured.	Calculated.
$c \wedge c$ (twin)	$0001 \wedge 000\bar{1}$	*71° 3′	
$c \wedge r$	$0001 \wedge 10\bar{1}1$	54 21	54° 28½′
$m \wedge r$	$10\bar{1}0 \wedge 10\bar{1}1$	35 39	35 31½

On examining this salt in convergent polarized light a uniaxial cross is seen whose arms are not black but a deep and brilliant blue, the character being negative. When examined in monochromatic red light the crystals are nearly isotropic, the double refraction being extremely weak and probably negative. In blue light, however, a distinct cross is seen accompanied by axial rings. This difference between red and blue explains the colored cross seen in white light. Sections parallel to the c axis show the deep peculiar blue characteristic of uniaxial bodies with the above mentioned optical properties.

$3CsBr \cdot 2AsBr_3$.—This salt was made in crystals up to $1\frac{1}{2}^{mm}$ in diameter. The forms observed are c, m, r and z This is the only salt of the series that has a rhombohedral habit and as the angle of the rhombohedron is nearly 90° the crystals look like cubes. Fig. 3 shows an ideal combination of r with m, z and c. This form was not observed as the crystals are

3.



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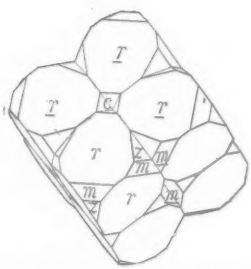


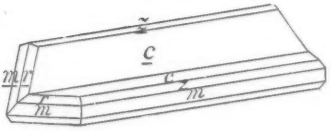
invariably twins. An ideal representation of the twinning is given in fig. 4. The r faces were so curved and striated that no exact measurements could be made from them.

		Measured.	Calculated.
$m \wedge z$	$01\bar{1}0 \wedge 01\bar{1}1$	*35° 23′	
$z \wedge z$	$10\bar{1}1 \wedge \bar{1}101$		89° 50′

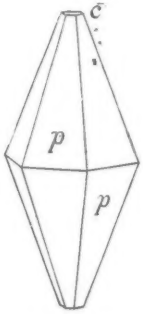
$3RbBr \cdot 2AsBr_3$.—This salt was made in small crystals, up to 2^{mm} in diameter. The forms observed were c, m and r. The crystals were made in two habits. When prepared with an excess of RbBr it separates in prismatic crystals which resemble the form of cæsium arsenious chloride, fig. 1. In one experiment by using an excess of $AsBr_3$ contact twins were obtained. Here the twinning plane is the unit rhombohedron as in fig. 2, but some of the faces are lengthened parallel to the edge between the two basal planes (fig. 5).

		Measured.	Calculated.
$c \wedge c$ (twin)	$0001 \wedge 0001$	70° 45′	70° 44′
$c \wedge r$	$0001 \wedge 10\bar{1}1$	54 40	54 38
$r \wedge m$	$10\bar{1}1 \wedge 10\bar{1}0$	*35 22	
$r \wedge z$	$10\bar{1}1 \wedge 01\bar{1}1$	48 14	48 7½
$m \wedge z$	$10\bar{1}0 \wedge 01\bar{1}1$	65 34	65 56

5.



6.



$3CsI.2AsI_3$.—This salt was made in beautiful crystals up to 3^{mm} in length. The forms observed are p and c. The habit is that of a steep doubly terminated hexagonal pyramid, with the basal planes small or wanting. Often the middle edges are rounded by oscillatory combinations of the pyramids giving rise to horizontal striations. There was no indication of a prism or of a rhombohedral development of the pyramidal faces.

		Measured.	Calculated.
$c \wedge p$	$0001 \wedge 20\bar{2}1$	*70° 49′	
$p \wedge p$	$20\bar{2}1 \wedge 20\bar{2}\bar{1}$	38 19	38° 22′
$p \wedge p$	$20\bar{2}1 \wedge 02\bar{2}1$	56 24½	56 21 34″

This salt is without optical anomalies and no pleochroism was observed.

$3RbI.2AsI_3$.—This salt was prepared in very small crystals, not over 1^{mm} in length. The forms observed were c, m and p. The habit is similar to fig. 6 but usually the middle edges are replaced by the faces of the prism m or are rounded by horizontal striations.

		Measured.	Calculated.
$p \wedge p$	$20\bar{2}1 \wedge 02\bar{2}1$	*56° 21′	
$c \wedge p$	$0001 \wedge 20\bar{2}1$	70 47	70°
$p \wedge m$	$20\bar{2}1 \wedge 10\bar{1}0$	19 12	20 56′

Optically, this salt shows anomalies. Basal cleavage plates between crossed nicols are not dark but light and remain so during revolution. In convergent light the locus of an optic axis is seen in the center of the field coinciding with the ver-

tical axis c. The bisectrix lying nearest this axis is that of least elasticity C. The salt is not, however, properly biaxial, the plane of the optic axes is sometimes parallel, sometimes perpendicular to the edge of the prism. Moreover this direction often changes from place to place in the same plate and at times no bar is seen, but a black dot in the center of the field surrounded by rings. Such behavior can be explained by supposing the crystal to be in a condition of internal strain. Sections parallel to the prism sometimes remain light between crossed nicols, sometimes extinguish at varying angles and show a slight pleochroism, the absorption being $\varepsilon > \omega$; the color a deep reddish orange.

In conclusion the author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the present investigation and to Prof. S. L. Penfield under whose direction the crystallography of these salts was investigated. The author is also indebted to Mr. L. V. Pirsson for aid in the optical description of these salts.

Sheffield Scientific School, March, 1893.

ART. XIII.—*On Mackintoshite, a new thorium and uranium mineral;* by WM. EARL HIDDEN: with analyses by W. F. HILLEBRAND.

History.—It is three years since an alteration product* of the new species here described was announced jointly, by the late James B. Mackintosh,† and the writer, under the name of "thoro-gummite." In the interim a most diligent search has been made at the locality in Llano County, Texas, to discover the mineral in quantity, and also, if possible, the parent mineral from which it was derived. In an endeavor to find some fragments of the unaltered mineral, I broke up nearly a kilogram of the thoro-gummite, with the result of finding less than one gram of a black mineral which, from the position it occupied *within* the thoro-gummite, we concluded must represent the original species. I note here that some irregular cores, of a dark brown translucent mineral, were also found but they proved to be very soluble and not essentially different from the enclosing thoro-gummite. They had a density of 4·50.

Some chemical tests, then made by the writer, proved the black mineral to be practically unaffected by hydrochloric or sulphuric acids and the density as then determined was 5·361.

* This Jour., vol. xxxviii, Dec., 1889, p. 480.

† He died on April 15, 1891; see this Journal, xli, 444.

Upon fusing a portion with sodium bisulphate a solution was obtained and it was thus found to be a silicate containing about 23 per cent of uranium oxide (calculated as UO_2), about 46 per cent of thoria and a small per cent of the "rare earths."

No further data were then obtained from the scant material in hand but its relation to thoro-gummite was made evident. It was among fresh shipments of the various thoria and yttria minerals, made direct from the locality (Llano County, Texas) that this mineral was again found and further analytical work made possible. The new material was unexpectedly found deeply embedded in massive cyrtolite and associated with fergusonite. None was found embedded in the new crystals and masses of thoro-gummite. Some fifty kilograms of the broken cyrtolite were thoroughly searched through with the result of finding only about two grams of *pure* material and this came mainly from one mass, which had a very thin coating of thoro-gummite. A few selected fragments had a specific gravity of 5·438, [one portion weighed 0·35 gram.] As the mineral was so scarce it was set aside to await an opportunity when it could be given careful investigation. Later, by using small quantities, the physical characters were made out as follows.

Description.—The mineral is opaque and black, but not quite so dull in luster as the associated black cyrtolite which it resembles to a very remarkable degree. A strong lens is necessary to distinguish the two. Its hardness is about 5·5. No trace of cleavage has been observed. Its fracture is minute sub-conchoidal to hackly. Density = 5·438 at 21° C. (for the material analyzed by Hillebrand, see beyond.) Its form, as is often evidenced by the thoro-gummite, is tetragonal and closely resembles zircon and thorite in habit and angle. Square prisms, sometimes 1^{cm} thick, with a simple pyramid are all the forms thus far observed. It also occurs massive, nodular and filling veins in cyrtolite and fergusonite embedded in a coarse pegmatite. Under the blowpipe, it is infusible but becomes fissured in all directions without intumescence or decrepitation.

In powder the mineral is not entirely decomposed by any one acid. Sulphuric acid attacks it quite strongly but the gelatinous silica set free protects it from further action. Hillebrand has observed however that if nitric acid is added, speedy and complete solution results.

Chemical Composition.—For the chemical investigation of this mineral I am indebted to Mr. W. F. Hillebrand, whose important contributions to the chemistry of uranium minerals are well known. I quote his report and analyses in full.

"Of the dull black mineral supposed by Mr. Hidden to be the parent of thoro-gummite but nine-tenths of a gram was available

for analysis after careful hand-picking under the lens. It was almost entirely free from recognizable impurity and had a density of 5·43 at 21·4° C.

In powder the mineral is not entirely decomposed by any one acid so far as the necessarily restricted tests indicated. Sulphuric acid attacks it quite strongly, but the gelatinous silica set free protects a portion from further action. The addition of nitric acid then, however, causes speedy and complete solution. This behavior is perhaps susceptible of a different explanation, namely, that the mineral is not homogeneous, but consists of two different substances the predominant one of which is decomposable by sulphuric acid, the other much less affected by it but when once it has been opened up by removal of the former is readily dissolved by nitric acid. Nitro-hydrochloric acid likewise dissolves it completely.

Considering that the limited sample had to be divided into three portions in order to estimate the constituents tabulated below, it is not perhaps surprising that the analysis should present a loss of three and one-half per cent. The presence of even the little phosphoric acid shown renders the analytical operations by which the silica and bases are determined extremely complicated, particularly when zirconia and yttria are present. Precipitates are then obtained which under similar conditions the other earth bases do not give, and thus separations and identifications are rendered more difficult and losses are almost inevitable. It is therefore not at all certain that the very considerable loss is to be sought in some constituent not enumerated; it is more probable that it should be distributed somewhat unevenly over a number of those given, silica and lead oxide excepted, they being without doubt nearly correct. The following observations, however, may be of importance in this connection. After sealing the tube in which was the sample serving for the estimation of the oxidizable constituents a slow but long continued evolution of gas was observed, just as in the case of most uraninites when similarly treated, but owing to the very small quantity of powder in the tube—only ·15 gram—it could not be proven that the gas was nitrogen and not CO_2. The latter it should not be, for thorogummite, the direct alteration product of the mineral, is free from it according to Hidden and Mackintosh's analysis. In any event its amount is probably very small.

With respect to the oxidizable constituents it was found to be impossible to secure complete solution of the powder in the tube even after several days' heating with dilute sulphuric acid, owing presumably to the above mentioned protective action of silica set free and of thorium sulphate thrown out. The amount of oxygen consumed indicated 16 per cent of oxidizable bases counted as UO_2; it may be, therefore, that all the uranium exists in that form and the iron in the ferrous state, as they are given in the analyses which follow. Of these *b* was made on a small sample selected grain by grain with the utmost care, but it was evidently not

much purer than the first lot. There is at most an indication that FeO, CaO, alkalies, P_2O_5 and perhaps some water arise from impurities. Titanium, manganese, and fluorine are not present in the mineral.

	a	*b*
SiO_2	13·90	13·92
UO_2	22·40	21·86†
ZrO_2?	·88	lost
ThO_2, Ce_2O_3?, La_2O_3, Y_2O_3 groups	45·30*	lost
	1·86	lost
PbO	3·74	3·92
FeO	1·15	‡
CaO	·59	·44
MgO	·10	·13
K_2O	·42	·70
$(Na, Li)_2O$	·68	·70
P_2O_5	·67	·46
H_2O above 100° C.	4·31	
H_2O below 100° C.	·50	·35
	96·50	

Thoro-gummite (H. & M.)	
SiO_2	13·085
UO_3	22·43
ThO_2	41·44
Al_2O_3	·965
Fe_2O_3	·845
$(Ce, Y)_2O_3$ etc.	6·69 (At. W. 135)
PbO	2·16
CaO	·41
P_2O_5	1·19
H_2O	7·88
Moisture	1·23
	98·325

Taken by themselves these results are incapable of translation through the medium of molecular weights into any precise formula, but they become of interest when compared with the accompanying analysis of thoro-gummite by Hidden and Mackintosh.§ It is then seen that the opinion of Mr. Hidden regarding the derivation of thoro-gummite from the present mineral was fully justified. It is in fact remarkable, considering the great molecular alteration that must have taken place, as determined by the totally different appearance of the two minerals, that so little loss of substance has taken place. Almost the sole change has consisted in an oxidation of uranous oxide and an increase in the hydration. These facts render not altogether safe the assumption above made that all uranium and iron in the new mineral exist there in the lower forms of oxidation, and they furthermore indicate that the black mineral itself may have already undergone oxidation and hydration without this being manifest to the eye—a supposition which is strengthened by the loss at 100° C. of half a per cent of water, and in fact by the intimate union which existed between the two minerals when received. Such material alteration without corresponding physical evidence of it seems to be common among uraninites. The original condition of the mineral may then have been one in which uranium and iron were entirely in the lower state of oxidation and in which

* The precipitate by potassium hydroxide was pure white after long action of chlorine. It may, however, have contained a trace of cerium.

† Would be slightly increased by uranium which was not separated from the earths.

‡ The estimation of iron miscarried, but the amount was unquestionably less than in *a*.

§ This Journal, xxxviii, 480, 1889.

water was possibly absent. It is to be hoped that opportunity may yet be afforded for a more thorough examination of this mineral, which though apparently allied to thorite and uranothorite, is distinguished from them chiefly by greater content in uranium and by a higher degree of basicity."

Discussion of Composition.—It may be of interest to add a few words as to the relation of this mineral to thoro-gummite, although in view of the loss of 3·5 per cent in the analysis there is an unavoidable element of doubt attached to any formulæ which may be deduced. However, if the larger proportion of the loss is considered as due to general losses, due to the small quantity of material used, the following suggestions as to the true composition of mackintoshite, may be made.

A comparison of the two analyses with that of thoro-gummite shows at once that the change has essentially been the further oxidation of the uranium (from UO_2 to UO_3) and the assumption of one molecule more of water. Thus, as $3SiO_2$, UO_3, $3ThO_2$, $6H_2O$ expresses well the composition of thoro-gummite, so $3SiO_2$, UO_3, $3ThO_2$, $3H_2O$ is very probably the formula of the new mineral. In both minerals about one fourth of the thoria is replaced by its equivalent in RO, RO_2, R_2O_3 which, if later proved to be a constant factor, should be expressed in the formula. Both the analyses seem to show that $3SiO_2$, UO_3, $3(\frac{3}{4}ThO_2, \frac{1}{4}RO)3H_2O$ expresses best the mineral analyzed.

That an anhydrous form occurs in nature, as is thought true of thorite, seems indeed most probable, this would then be $3SiO_2$, UO_3, $3ThO_2$; which requires: Thoria 63·67 per cent, silica 14·47 per cent, uranous-oxide 21·86 per cent = 100. As a basic silicate, in condensed form, it could be expressed thus: $3Si$, $4(U, 3Th)O_{14}$.

In the calculations of the molecular ratios the alkalies and magnesia have been neglected as non-essential and the phosphoric acid has been considered as combined with the excess of uranium; this gives the following results.

	Per cent.		Mol. wt.		Molec. ratios.		
SiO_2	= 13·90	÷	60	= 23·167	= 5·048	=	3
UO_3	22·40		272	8·231	1·083		1
ThO_2	45·30		264	17·159	2·256		
$(Yt, La)_2O_3$	1·86		288	·645			3
ZrO_2	0·88		122	·721			
PbO	3·74		222	1·684	5 700	0·750	
FeO	1·15		72	1 597			
CaO	0·59		56	1·053			
H_2O	4·31		18	23·944	3·150		3

The above ratios are as close as could reasonably be expected.

It will be interesting to compare the molecular ratios of the theoretical mineral with those found for the analyses of mackintoshite and thoro-gummite and to notice the sharp relationships brought out.

Mackintoshite.

Theory.		Molec. ratio.	Found.	Molec. ratio.	Error.
$3SiO_2$	= 13·87% =	23·11	13·90% =	23·16 =	+0·03%
$1UO_2$	20·95	7·70	22·40	8·23	+1·45
$3ThO_2$	61·02	23·11	60·35	22·86	−0·67
$3H_2O$	4·16	23·11	4·31	23·94	+0 15

Thoro-gummite.

Theory.		Molec. ratio.	Found.	Molec. ratio.	Error.
$3SiO_2$	= 13·16% =	21·93	13·08% =	21·81 =	−0·08%
$1UO_2$	21·05	7·31	22·43	7·47	+1·38
$3ThO_2$	57·89	21·92	57·60	21·82	−0·29
$6H_2O$	7·90	43·83	7·88	43·77	−0·02

In conclusion I wish to reiterate the purely conjectural character of the above tabulated results and to repeat the wish of Dr. Hillebrand that more of this new mineral may be found so that its true composition and formula may be known beyond all question or doubt. That the mineral is more basic than either thorite or uranothorite* seems at once obvious.

I propose the name of mackintoshite for this new species in honor of the able chemist, the late Mr. James Buckton Mackintosh of New York City. The name seems peculiarly appropriate because of the large amount of valuable work which he did in mineralogy and especially since the mineral contained an earth—thoria—to which he had given an especial study.

* Lindström's analysis of uranothorite gives, by calculation, the ratios of 1 : 1 : 2 for silica, bases and water and shows no apparent ratio for the uranium to the other bases.

ART. XIV.—*Alnoite containing an uncommon Variety of Melilite;* by C. H. SMYTH, Jr.

IN an earlier paper* the writer described a small dike occurring in a fault fissure at Manheim, N. Y. The rock examined was much decomposed, but showed under the microscope abundant olivine, dark brown mica, magnetite, and perofskite, with considerable quantities of alteration products. Upon this mineralogical composition was based a determination of the rock as peridotite. Some sections showed, in addition to the minerals named, another constituent, "of imperfect lath shape," in color white, green or brown, and with a marked fibrous structure perpendicular to the longer axis. The structure in some of the laths resembled the peg structure of melilite, and suggested that they might belong to this species; but their optical properties, notably the yielding of second order interference colors, seemed to preclude the acceptance of such a supposition.

Recently, however, some sections have been prepared from fresher material, and these show that this first supposition in regard to the nature of the mineral was correct. It is melilite, though in one respect quite different from that mineral as usually described.

In the fresh material the laths are much more abundant than in the altered rock, and possess a more definite and uniform character. Instead of the fibrous structure they show a very perfect peg structure, while the optical properties, with a single marked exception, agree closely with those generally ascribed to melilite. On the other hand, in the weathered rock from which the first sections were made the melilite is so greatly altered that it gives very imperfect evidence of its original character. These sections afford a good illustration of the rule stated by Stelzner† in regard to other rocks of a similar character: the melilite is often completely decomposed while the olivine remains quite fresh. Adams,‡ also, has stated that in the alnoite of Ste. Anne, Canada, "the melilite is well seen only in sections of the fresh rock," being no longer easily recognizable "when the rock is decomposed to any considerable extent."

* A Third Occurrence of Peridotite in Central New York, this Journal, III, xliii, p. 322.

† Stelzner, A.: Ueber Melilith und Melilithbasalte, Neues Jahrbuch für Mineralogie, etc., Beilage-Band II, p. 388.

‡ Adams, F. D.: On a Melilite-bearing Rock (Alnoite) from Ste. Anne de Bellevue, near Montreal, Canada; this Journal, III, xliii, p. 278.

In the fresh rock the laths show much variation in size, averaging perhaps about ·25^{mm} in length, but often reaching ·5^{mm}. Their outline is sometimes irregular, sometimes sharply rectangular. Basal sections of the mineral are not common; when seen they usually have an imperfect quadratic shape. The most conspicuous feature of the laths is the peg structure, consisting of small peg-like bodies, usually starting from the basal planes, and extending partly or wholly across the lath. This structure is very unevenly distributed, being quite absent in some cases, and in others extending through the entire lath. Again, it may be confined to one-half of a lath, while the other half is quite free. Sometimes the pegs lie in the central portion of the lath, and do not extend to either face; they may also be elongated parallel to the long axis of the lath. As a rule the outline of the pegs is rather irregular, though it not uncommonly approaches the sharpness and symmetry of Stelzner's figures.* In the course of alteration the peg structure becomes obscured by the development of a fibrous structure, and the outlines of the laths lose sharpness, quickly destroying the characteristic appearance of the mineral.

Many laths show no trace of cleavage, but in others it manifests itself by a single crack parallel to the long axis. Less often two or more cracks appear. In the earlier stages of decomposition the cracks are sometimes accentuated by the formation of alteration products.

In the thinnest parts of sections the melilite is colorless, elsewhere it has a decided yellowish tint. Compared with melilite from other localities its mean index of refraction is perhaps a little lower, while the double refraction is rather stronger, a yellow interference color being obtained in moderately thin sections. But while differing very slightly from other melilites in these respects, it shows a marked divergence in another property. Examination of the laths with a gypsum plate shows that their long axis is the direction of greatest elasticity, and the short axis the direction of least elasticity. As the mineral is tabular parallel to the basal pinacoid, this gives for its optical orientation $a = \mathfrak{a}$ and $\dot{c} = \mathfrak{c}$, $\omega < \varepsilon$ and the mineral is positive. While this is true of a large proportion of the melilite, it is not invariably the case, for laths are occasionally found in which the mineral is negative. More common is the occurrence of laths, which, though consisting chiefly of positive material, have patches of a negative character scattered through them.

The negative character of melilite as a rock constituent has been so generally regarded as constant that any exception to

* Op. cit., Taf. VIII, fig. 4.

the rule is of particular interest. Artificial melilite of positive character has been described by Vogt* and by Bodländer ;† but even so recent a work as the third edition of Rosenbusch's "Mikroskopische Physiographie der petrographisch wichtigen Mineralien," though implying the probable existence of a positive molecule in ordinary melilite, does not definitely state that the mineral is sometimes positive in rocks. As a rock constituent melilite of a positive character has been mentioned, so far as the writer knows, only by Becke.‡ He refers to two nepheline basalts containing melilite of positive character; and as an explanation states that "man wird nicht fehlgehen, wenn mann annimmt, das die gesteinbildenden Melilithe isomorphe Mischungen von zwei Endgliedern seien, von denen das eine mit negativer Doppelbrechung wohl im vesuvischen Humboldtilith vorliegt, während das positive noch unbekannt ist." This explanation is in accord with the facts observed in the Manheim rocks, as well as with the observations of Vogt, who was led to a similar conclusion in regard to the artificial melilite. Bodländer, however, holds that this view is inconsistent with the results of analyses of artificial melilite, and concludes that the mineral is positive when it contains a large amount of magnesium.§

With the view of obtaining further evidence as to the occurrence of positive melilite, sections of five other rocks containing the mineral have been carefully examined. The rocks are melilite basalts from Wartenberg, Bohemia, and Hochbohl, Württemberg; leucitite from Capo di Bove, Italy; and alnoites from Alnö, Sweden, and Ste. Anne, Canada. All of these localities with the exception of the last, are so noted as to be almost classic. The sections of the first three rocks were prepared by Voigt and Hochgesang in Göttingen. For the sections of the two alnoites, as well as for other assistance, the writer is indebted to Professor George H. Williams.

While in all of these rocks the ordinary negative melilite predominates, in two of them, the melilite basalt from Wartenberg and the alnoite from Alnö, the positive variety exists to some extent. In both rocks it forms entire laths like those in the Manheim rock, being particularly abundant in the basalt.

Although, of course, it does not follow that in an examination of a larger number of rocks as great a proportion would

* Vogt, J. H. L.: Studier over Slagger, Stockholm, 1884; also Beiträge zur Kenntniss der Gesetze der Mineralbildung in Schmelzmassen und in den neovulkanischen Ergussgesteine, Christiania, 1891.

† Bodländer, G.: Entstehung von Melilith beim Brennen von Portland-cement, Neues Jahrbuch für Mineralogie, etc., 1892, I. p. 53.

‡ Becke, F.: Optischer Charakter des Melilith als Gesteinsgemengtheil, Tschermak's Mittheilungen, xii, p. 444.

§ Op. cit. p. 56.

be found to contain positive melilite, still it is probable that this variety of the mineral has a greater distribution than has heretofore been supposed. Its occurrence in such abundance in the Manheim dike adds interest to a rock in itself so rare as to be worthy of special note.

Of the other minerals in the rock the olivine, magnetite, and perofskite show no unusual features and require no description other than that previously given.

The mica, on examination in convergent light, proved to be biotite. In view of the nature of the rock this result was hardly to be expected, and it is probable that anomite is also present, though not yet identified.

Upon the basis of its mineralogical composition, and from a comparison with a specimen from the type locality* the rock must be classed as alnoite. The only respect in which it differs very markedly from the rock at Alnö is in the almost complete absence of pyroxene. With this exception, sections from the two localities are nearly identical in appearance.

The same difference exists in greater degree between the Manheim rock and the one other melilite rock thus far described from this country—the alnoite of Ste. Anne, Canada. The latter rock also contains nepheline which has not been found in the Manheim alnoite. Still, in spite of these differences, the rocks are so closely related that there can be no error in classing them together.

Hamilton College, Clinton, N. Y., April, 1893.

ART. XV.—*On Canfieldite a new Germanium Mineral and on the Chemical Composition of Argyrodite;* by SAMUEL L. PENFIELD.

IT is with great pleasure that the author is able to announce the discovery of a new mineral containing germanium and to record the occurrence of this rare and interesting element from a new locality. The credit of this is due in great measure to the keen mineralogical interest of Mr. Frederick A. Canfield of Dover, N. J., to whom, while on a business trip in Bolivia, South America, some specimens of this mineral were given as samples of a rich and unknown silver ore, by friends connected with the mining industry. These were brought to the writer for identification and he takes great pleasure here in acknowledging his indebtedness to Mr. Canfield and in expressing his

*Törnebohm, A. E.: Melilitbasalt fraan Alnö; Geol. Fören i Stockholm Förhandl., 1882, vi, No. 76, p. 240.

thanks to him for the liberality with which he has placed an abundant supply of this valuable material at his disposal. It is in acknowledgment of these services that the mineral has been named after him.

It is unfortunate that at the present no further information can be given concerning the exact locality and mode of occurrence, but from inquiries that have been set on foot by Mr. Canfield it is hoped that full data concerning these points will be given later.

When the mineral was brought to the writer, attempts made to identify it at once showed that it was not one of the ordinary silver minerals. Thus in the open tube it gave a reaction for sulphur but no sublimate. In the closed tube with a Bunsen burner flame only a slight sublimate of sulphur, but at a higher temperature with a blowpipe flame the sulphur increased, while nearer the assay a pale yellow sublimate formed, which became lighter on cooling. On examining this with a lens it was found to consist of minute globules most of which were nearly colorless but some were yellow. Boiling concentrated nitric acid was found to attack and oxidize the mineral very slowly. On charcoal in the oxidizing flame it fused readily and gave almost immediately a pure white sublimate near the assay, but no color to the flame. On continued blowing this sublimate moved farther out, assuming a color which varied from greenish to brownish yellow, for the most part lemon yellow, while the assay changed to a pure silver bead. On examining the coating more minutely with a lens it was seen to have a peculiar smooth appearance, as if it had fused on the surface of the charcoal, while scattered about nearer the assay were numerous small transparent to milk white globules, along with minute globules of silver. These tests led to the suspicion that the mineral might possibly contain germanium and a comparative test, made with argyrodite on charcoal, gave exactly the same results. It is to be noted here that while Richter* describes very minutely the reactions which argyrodite gives on charcoal he does not mention the smooth surface of the coating or the formation of the fused globules which form so characteristic and useful a test for the identification of germanium. In order to prove beyond all doubt the identity of the element thus indicated with germanium the properties of the element as given by Winkler† were studied, a series of careful qualitative tests were made together with the formation of most of the important compounds mentioned by him. Thus a sulpho-salt, soluble in alkaline solutions like those of the tin, arsenic and antimony group, was prepared,

* Quoted by Weisbach, Jahrb. f. Min., 1886, ii, p. 67.
† Journ. f. prakt. Chem., xxxiv, 1886, p. 177.

from which solution the addition of acid, especially in large excess, precipitated a white sulphide. On heating some of this sulphide in a tube through which a current of hydrogen was passed, small glittering scales of GeS, in luster resembling hematite, were formed just beyond the ignited material. These on examination with the microscope in transmitted light were found to be dark brown in color. Although not mentioned by Weisbach* it was noted that these were strongly pleochroic, the direction of greatest absorption being at right angles to the longest axis of the plates. By continued and higher heating a still further reduction took place and metallic germanium was deposited as a crystalline sublimate on the walls of the tube. Microscopic examination showed this sublimate to consist of small gray-white octahedral crystals of magnificent metallic luster. They were found to be insoluble in hydrochloric acid but were readily dissolved by aqua regia. These results agree exactly with those given by Winkler and the identity was still further confirmed by the entire behavior of the element and by other results which will be given in the course of this article.

The physical properties of this new mineral are as follows: Crystallization isometric. Among the specimens furnished by Mr. Canfield were two which were well crystallized. One of these consisted of a group of unmistakable octahedral crystals, averaging about 7^{mm} in axial diameter, but which were too rough for measurement on the goniometer. Their edges were sometimes truncated by the dodecahedron, while some were twinned about an octahedral face. The other specimen contained equally large but less isolated crystals, the luster of whose faces was good and one of the crystals, showing the four upper faces of an octahedron, with edges truncated by the dodecahedron was measured on the reflecting goniometer as follows:

$111 \wedge \bar{1}11$	= 70°	0′			
$\bar{1}11 \wedge \bar{1}\bar{1}1$	= 70	29			
$\bar{1}\bar{1}1 \wedge 1\bar{1}1$	= 70	14	$111 \wedge \bar{1}\bar{1}1$	= 108°	57′
$1\bar{1}1 \wedge 111$	= 70	8	$1\bar{1}1 \wedge \bar{1}11$	= 109	3
Calculated,	70	32	Calculated,	109	28

The reflections of the signal were moderately good and considering a slight rounding of the faces the measurements agree as closely to those of the octahedron as could be expected. The dodecahedral faces were too uneven to yield a distinct reflection. These crystals were tested and found to give the characteristic reactions for germanium. The fracture is irregular to small conchoidal. Extremely brittle. Hardness about 2·5. The specific gravity of two distinct, massive fragments,

* Quoted by Winkler, loc. cit., p. 215.

weighing about five and six grams each, carefully taken on a chemical balance after boiling in distilled water, was found to be 6·2662 and 6·2657 respectively, the temperature being 25° C. The specific gravity of the fragment containing the crystal that was measured and weighing over 22 grams was found to be 6·270. The luster is brilliant metallic. The color black with a blueish to purplish tone. The streak is grayish black, somewhat shiny. The chief pyrognostic properties have already been given. In addition the fusibility at about 1½ to 2 should be noted. The fused transparent globules which were observed on charcoal are probably GeO_2. Some of the oxide separated from the quantitative analysis was tested on charcoal as follows: In the oxidizing flame it fused with bubbling to a transparent, glassy globule, giving no coating. By continued heating in the reducing flame it darkened and gave slowly a pure white sublimate. The yellow coating obtained on charcoal from the mineral was probably a mixture of oxide and sulphide of germanium. The fused globules, which were observed near the assay in the closed tube are GeS_2 or possibly some oxysulphide. Argyrodite, when tested in the closed tube, gives at first a black sublimate, which as stated by Richter,* looks exactly like mercuric sulphide and undoubtedly is that substance. On intense heating before the blowpipe there formed farthest up on the tube a sublimate of sulphur, next followed the black ring of mercuric sulphide, neither of which increased perceptibly by continued heating, while nearest the assay the nearly colorless globules of GeS_2 were deposited. On breaking off the lower end of the tube, driving off the sulphur and mercuric sulphide by gentle heat and then roasting the globules in a current of air, SO_2 was given off while the germanium oxide collected into a fused mass but was not volatilized. Regarding the association of canfieldite with other minerals, all that can be said is that the specimens are remarkably pure, only slight quantities of pyrite, sphalerite and kaolin being attached to them.

It having been shown that the mineral was essentially a sulpho-salt of germanium and silver, the following method was adopted for analysis. A weighed quantity, about two grams, was oxidized by concentrated nitric acid, the operation requiring from one to two hours on the water bath. After the oxidation was complete the excess of nitric acid was removed by evaporation. The residue was then dissolved in warm water slightly acidified with nitric acid, and after filtering off a slight trace of insoluble residue the silver was precipitated by hydrochloric acid, filtered and weighed. In the

* Quoted by Weisbach and Winkler. Loc. cit.

filtrate the sulphur was precipitated as barium sulphate, which was purified by fusion with sodium carbonate, reprecipitated and weighed. For the determination of germanium another portion of two grams was oxidized by nitric acid with the addition of a little sulphuric acid. After removal of the large excess of nitric acid by evaporation, the residue was dissolved in warm water, with addition of some nitric acid if necessary, the silver precipitated with ammonium thiocyanate and removed by filtration. The filtrate contained the germanium together with no acid which forms with it a volatile compound. It was evaporated in a platinum dish, the nitric acid present serving to completely destroy the ammonium thiocyanate, and the excess of sulphuric acid was finally driven off by heating. The residue thus obtained was covered with a little strong ammonia into which hydrogen sulphide was conducted. Under this treatment the germanium oxide dissolved, while all heavy metals, except those which form sulpho-salts soluble in ammonium sulphide, were left undissolved. In this particular case a very small quantity of a black sulphide remained; it was filtered off, ignited and weighed. It is assumed to be a mixture of zinc and iron oxides, resulting probably from admixed sphalerite and pyrite. The filtrate containing the germanium was collected in a weighed platinum crucible and evaporated on the water bath. The residue was oxidized by strong nitric acid, the excess of which was removed by evaporation. The crucible, placed inside of a porcelain one, was then ignited, gently at first, finally to the full extent of a ring burner, then weighed and the germanium determined as GeO_2. On further ignition the weight was found to be constant, nor did it change by heating to full redness. When heated in a current of ammonia and air, to remove sulphuric acid, the weight diminished very little; thus in one experiment it fell from 0·1535 to 0·1525 grs., showing that a gentle ignition is sufficient to practically expel all of the sulphuric acid. By heating to a bright redness in a current of ammonia and air the germanium oxide suffered reduction to the metallic state. To show that the germanium oxide was pure and especially to prove the absence of arsenic and antimony the following tests that were made may be mentioned. Rather large quantities of the mineral, when roasted in the open tube gave no sublimate. An acid solution of the oxide gave upon addition of hydrogen sulphide a white precipitate, which when collected on a filter showed only a pale tinge of yellow. Also the oxide obtained in the analysis when dissolved and brought into a Marsh apparatus gave only a most minute and unweighable blackening on the walls of the tube, which on ignition in the air changed to a scarcely perceptible white oxide resembling

antimony. As the mineral dissolves completely in nitric acid tin cannot be present. These results therefore showed that the germanium was satisfactorily pure. Another method of analysis in which everything was determined in one portion is as follows: Solution of the mineral in nitric acid, precipitation of the silver with hydrochloric acid, of the sulphur with barium nitrate, removal of the excess of chlorine and barium in one operation with silver nitrate and sulphuric acid, final removal of the silver by ammonium thiocyanate and determination of the germanium in the filtrate as above.

The result of the analysis gave the following figures:

				Average.	Deducting impurities.	Theory for Ag_8GeS_6
S	17·03	17·04		17·04	17·10	17·06
Ge	6·51	6·52	6·61	6·55	6·57	6·42
Ag	76·01	76·09		76·05	76·33	76·52
Fe, Zn	·14	·16	·10	·13		
Insol.	·29			·29		
				100·06	100·00	100·00

The formula of the mineral is evidently Ag_8GeS_6 or $4Ag_2S \cdot GeS_2$. The agreement of the analysis with the theory as will be noticed is reasonably close.

Winkler made the following analysis of argyrodite, from which he derived the formula Ag_6GeS_5 or $3Ag_2S \cdot GeS_2$.

	Analysis by Winkler.	Theory for $Ag_6Ge_2S_5$	Theory for Ag_8GeS_6	Atomic weights.
S	17·13	18·21	17·06	32
Ge	6·93	8·23	6·42	72·32
Ag	74·72	73·56	76·52	107·7
Hg	·31			
Fe	·66			
Zn	·22			
	99·97	100·00	100·00	

It will be noticed that Winkler's analysis agrees much more closely with the theory for Ag_8GeS_6, especially in respect to the sulphur and germanium, than with the formula advanced by him. It seems probable, therefore, that the two minerals have the same chemical composition, but since Weisbach has shown that argyrodite is monoclinic and since canfieldite is isometric, they cannot be identical.

In order to investigate this point more closely it seemed desirable to make a new analysis of argyrodite by the same methods which had been used for canfieldite. The material was very carefully selected from an excellent specimen of the

Freiberg argyrodite in the collection of Prof. Brush. The specific gravity was determined in two ways. Some larger fragments, weighing about two grams, gave on the chemical balance in distilled water 6·149 and the smaller ones gave by use of the pycnometer 6·162. These results, though somewhat higher than those given by Winkler and Weisbach, which were 6·085–6·111, are still considerably lower than the specific gravity of canfieldite. The result of the analysis is as follows:

			Average.
S	16·97		16·97
Ge	6·67	6·62	6·64
Ag	75·57	75·53	75·55
Hg	·34		·34
Fe, Zn	·24		·24
			99·74

It will be seen that this analysis agrees remarkably well with that of Winkler, the only essential difference being that the silver is somewhat higher and the iron and zinc are lower. This suggests that these latter are impurities, resulting from the presence of a slight admixture of pyrite and sphalerite, both of which are associated with the mineral. In regard to the mercury, since this element has never been known to occur otherwise at Freiberg, it is probable that it replaces silver. If we now recalculate these analyses, excluding the iron and zinc with sufficient sulphur to form pyrite and sphalerite, and replacing the mercury by its equivalent in silver, we obtain the following:

Canfieldite.	Argyrodite, Winkler.	Argyrodite, Author.	Theory for Ag_8GeS_6
17·10	16·56	16·83	17·06
6·57	7·05	6·69	6·42
76·33	76·39	76·48	76·52
100·00	100·00	100·00	100·00

From the consideration of these results there can be no doubt that canfieldite and argyrodite have the same chemical composition, which is Ag_8GeS_6. It is evident therefore that we have here a case of dimorphism, for both the crystalline forms and the specific gravities indicate that the minerals are distinct.

Laboratory of Mineralogy and Petrography,
Sheffield Scientific School, June, 1893.

ART. XVI.—*Epeirogenic Movements associated with Glaciation;* by WARREN UPHAM.

GEOLOGY is indebted to Gilbert in his monograph, "Lake Bonneville," for the terms *epeirogeny* and *epeirogenic*, designating the broad movements of uplift and subsidence which affect the whole or large portions of continental areas or of the oceanic basins. These terms are distinguished from *orogeny* and *orogenic*, which denote the folding, faulting, and upheaval of limited tracts as mountains and mountain ranges, forming narrow belts as compared with the extensive plateaus of the continents. Epeirogenic uplifts and depressions, except in areas of contemporaneous orogenic disturbance, take place apparently by gentle monoclinal or quaquaversal tilting of the marginal or outer parts of the broad regions affected, and exhibit a very gradual change in altitude from the central parts of those regions to the undisturbed surrounding areas. In the region of Lake Agassiz and of the Laurentian lakes, whose epeirogenic elevation after the recession of the ice-sheet has been well ascertained in its southern part by levelling and is found to vary from a few inches to somewhat more than five feet per mile of differential uplift from south to north, the movement has been so gradual that the continuity of the glacial lake beaches remains perfect, with no dislocations to indicate any faulting of the underlying bed-rocks.

Especial interest pertains to the epeirogenic movements of the Quaternary era from their relationship to the accumulation and departure of the Pleistocene ice-sheets, which was first pointed out by Dana in his presidential address before the American Association in 1855, as published in this Journal the following year. By reasoning from the prevalence of fjords in all glaciated regions and showing that these are valleys eroded by streams during a formerly greater elevation of the land previous to glaciation, and from the marine beds of the St. Lawrence valley and basin of Lake Champlain belonging to the time immediately following the glaciation, it was announced that the formation of the drift on this continent was attended by three great continental movements: the first upward, during which the ice-sheet was accumulated on the land; the second downward when the ice-sheet was melted away, and the third, within recent time, a re-elevation, bringing the land to its present height. With the moderate depths of the fjords and submarine valleys then known, the amount of preglacial elevation which could be thus affirmed was evidently too little to be an adequate cause for the cold and snowy climate pro-

ducing the ice-sheet. The belief that this uplift was 3,000 feet or more, giving sufficiently cool climate, as Prof. T. G. Bonney has shown, to cause the ice accumulation, has been only reached within the past few years by Spencer, LeConte, Hilgard, and the present writer, through the discoveries by soundings of the U. S. Coast Survey, that on both our Atlantic and Pacific coasts submarine valleys evidently eroded in late Tertiary and Quaternary time reach to profound depths, 2,000 to 3,000 feet below the present sea level.*

Although the adequacy of the preglacial epeirogenic uplift of this continent to produce its Pleistocene ice-sheet was tardily recognized and cannot yet be said to be accepted by all American glacialists, it was distinctly claimed by Dana in 1870 that the Champlain subsidence of the land beneath its ice-load, supposing it to have been previously at a high altitude, must have brought climatic conditions under which the ice would very rapidly disappear. The depression would be like coming from Greenland to southern Canada and New England. In Professor Dana's words: "Such an extended change of climate over the glacier area was equivalent in effect to a transfer from a cold icy region to that of a temperate climate and melting sun. The melting would therefore have gone forward over vast surfaces at once, wide in latitude as well as longitude."†

Such explanations as these accounting for the gradual accumulation and comparatively rapid dissolution of the North American ice-sheet are also found to be applicable to the ice-sheets of other regions. The fjords of the northern portions of the British Isles and of Scandinavia show that the drift-bearing northwestern part of Europe stood in preglacial time 1,000 to 4,000 feet higher than now, while on the other hand late glacial marine beds and strand lines of sea erosion testify that when the ice disappeared the land on which it had lain was depressed 100 to 600 feet below its present height, or nearly to the same amount as the Champlain depression in North America. Again, just the same evidences of abundant and deep fjords and of marine beds overlying the glacial drift to heights of several hundred feet above the sea are found in Patagonia, as described by Darwin and Agassiz. On these three continental areas, the widely separated chief drift-bearing regions of the earth are found to have experienced in connection with their glaciation in each case three great epeirogenic movements of similar character and sequence, first, a

* Detailed notes of these submerged valleys are presented in my payer "On the Cause of the Glacial Period," Am. Geologist, vol. vi, pp. 327–339, Dec., 1890.

† Trans. Conn. Acad. of Arts and Sciences, vol. ii, 1870, p. 67. Compare this Journal, III, vol. x, pp. 168–183, Sept., 1875.

great and comparatively long continued uplift, which in its culmination appears to have given a high plateau climate with abundant snowfall forming an ice-sheet, whose duration extended until the land sank somewhat lower than now, leading to amelioration of the climate and the departure of the ice, followed by re-elevation to the present level. The coincidence of these great earth movements with glaciation naturally leads to the conviction that they were the direct and sufficient cause of the ice-sheets and of their disappearance; and this conclusion is confirmed by the insufficiency and failure of the two other chief theories which have been advanced to account for the Glacial period.

During ten or fifteen years next following the publication of Dr. James Croll's very valuable work, "Climate and Time," and of the equally grand work by Prof. James Geikie, "The Great Ice Age," a quite general opinion among American glacialists favored the astronomical theory of the causes of glaciation which these authors so ably advocated. But in later years a similarly general opinion among us sets against that theory because of the uniqueness and the demonstrated geologic recency of the Glacial period; and therefore for a time some, who were specially impressed with the low level of our continent during the maximum and wane of its glaciation, looked with careful inquiry toward the doctrine of changes in latitude and in the position of the earth's poles, which was set forth in 1863 by Sir John Evans, with the suggestion that it might explain the remarkable Pleistocene changes of climate. Within the past two years, however, the brilliant discoveries by Dr. S. C. Chandler* of the periods and amounts of the observed variations of latitude, showing them to be in two cycles respectively of twelve and fourteen months, with no appreciable secular change, forbid reliance on this condition as a cause, or even as an element among the causes, of the Ice age. The second of these theories is out of the field, and the first, even in the modified form given to it by Wallace in "Island Life," cannot be admitted, in the opinion of most American students of this subject, when we find that the Ice age ended probably only 6,000 to 10,000 years ago.

The epeirogenic movements of the countries which became glaciated were only a portion of wide-spread oscillations of continental areas during the closing part of Tertiary time and the ensuing much shorter Quaternary era. Not only was northwestern Europe uplifted thousands of feet, but probably all the western side of Europe and Africa shared in this movement, of which we have the most convincing proof in the

* Astronomical Journal, vol. xii, pp. 57–62, 65–72, and 97–101, Aug. 4 and 23, and Nov. 4, 1892.

submerged channel of the Congo, about four hundred miles south of the equator. From soundings for the selection of a route for a submarine cable to connect commercial stations on the African coast, Mr. J. Y. Buchanan* found this channel to extend eighty miles into the ocean to a depth of more than 6,000 feet. The last twenty miles of the Congo have a depth from 900 to 1,450 feet. At the mouth of the river its width is three miles and its depth 2,000 feet. Thirty-five miles off shore the width of the submerged channel or cañon is six miles, with a depth of about 3,450 feet, its bottom being nearly 3,000 feet below the sea bed on each side. Fifty miles from the mouth of the river the sounding to the submarine continental slope is nearly 3,000 feet, while the bottom of the old channel lies at 6,000 feet. This very remarkable continuation of the Congo valley far beneath the sea level is like those of the Hudson and St. Lawrence rivers, and like numerous submerged valleys on the coast of California; but the Congo reaches to a greater depth than these of North America, and even exceeds the Sogne fjord, the longest and deepest in Norway, which has a maximum sounding of 4,080 feet. Another deep submarine valley, called the "Bottomless Pit," having soundings of 2,700 feet, is described by Buchanan on the African coast 350 miles north of the equator, and he states that a similar valley exists in the southern part of the Bay of Biscay. These observations show that within very late geologic time probably almost the entire Atlantic side of the eastern continent has been greatly uplifted, attaining as high an altitude as that which A. C. Ramsay and James Geikie conjectured as a possible cause of the frost-riven limestone agglomerates of Gibraltar.†

Likewise the tropical portions of the western continent, the West Indies, and the smaller islands of the Caribbean region, appear to have shared the epeirogenic disturbances which were associated with the glaciation of the northern and southern parts of this continent, as is well brought out by the recent studies and discussions of the geology of Barbados island by A. J. Jukes-Browne and J. B. Harrison,‡ and by the close relationship of the Pacific and West Indian deep sea faunas on the opposite sides of the Isthmus of Panama, made known through dredging by Alexander Agassiz.§ This testimony, indeed, with that of Darwin, L. and A. Agassiz, and others, of very recent, extensive, and deep subsidence of the western

* Scottish Geographical Magazine, vol. iii. 1887, pp. 217–238.

† Quart. Jour. Geol. Soc., vol. xxxiv, 1878, pp. 505–541.

‡ Quart. Jour. Geol. Soc., vol. xlvii, 1891, pp. 197–250.

§ Bulletin Mus. Comp. Zool. at Harvard College, vol. xxi, pp. 185–200, June, 1891.

coast of South America, apparently however continuing for no long time, lends much probability to the supposition that the low Panama isthmus was somewhat deeply submerged for a geologically short period contemporaneous with epeirogenic uplifts of the circumpolar parts of this continent both at the north and south, whereby the effects of high altitude in covering the northern and southern high areas with ice-sheets were augmented by the passage of much of the Gulf Stream into the Pacific Ocean.

The end of the Tertiary era and the subsequent Glacial period have been exceptionally characterized by many great oscillations of continental and insular land areas. Where movements of land elevation have taken place in high latitudes, either north or south, which received abundant precipitation of moisture, ice-sheets were formed; and the weight of these ice-sheets, as was first pointed out by Jamieson, seems to have been a chief cause, and often probably the only cause, of the subsidence of these lands and the disappearance of their ice. But the original sources of the energy displayed in the earth-movements of uplift preceding glaciation, and why this has been so extensively developed during the Quaternary era, are very difficult questions which it is not the purpose of this paper to consider, since I have attempted elsewhere to answer them, in an appendix of Wright's "Ice Age in North America." It may be properly noted, however, that the explanations mentioned are entirely consistent with Dana's teaching that the great continental and oceanic areas have been mainly permanent from very early geologic times.

Two formidable objections to this view that the accumulation of the Pleistocene ice-sheets was preceded and caused by great epeirogenic elevation deserve careful attention. The first consists in an approximate identity of level with that of to-day having been held by many drift-bearing areas at a time very shortly preceding their glaciation. This is clearly known to have been true of Great Britain and of New England. Near Boston, for example, my observations of fragments of marine shells in the till of drumlins in or adjoining the harbor prove for that tract a preglacial height closely the same as now at so late a time that the molluscan fauna, of which we have a considerable representation, comprised only species now living. In respect to this objection, it must be acknowledged that the preglacial high elevation which I think these areas experienced was geologically very short. With the steep gradients of the Hudson, of the streams which formed the now submerged channels on the Californian coast, and of the Congo, these rivers, if allowed a long time for erosion must have formed even longer and broader valleys than the still

very impressive troughs which are now found on these submarine continental slopes. But the duration of the epeirogenic uplift of these areas on the border of the glaciation for the Hudson, beyond it for the Californian rivers, and near the equator in western Africa, can scarcely be compared in its brevity with the prolonged high altitude held during late Tertiary and early Quaternary time by the Scandinavian peninsula and by all the northern coasts of North America from Maine and Puget Sound to the great Arctic archipelago and Greenland. The abundant long and branching fjords of these northern regions, and the wide and deep channels dividing the many large and small islands north of this continent, attest a very long time of preglacial high elevation there. At the time of culmination of the long continued and slowly increasing uplifts at the north, they seem to have extended during a short epoch far to the south, coincident with the formation of ice-sheets in high latitudes. But when these lands became depressed and the ice burden of the glaciated countries was removed, they in some instances, as in Great Britain and New England, returned very nearly to their original levels beautifully illustrating the natural condition of equilibrium of the earth's crust, which Dutton has named *isostasy*, that when not subjected to special and exceptional stresses it acts as if floating on a heavier plastic and mobile interior.

Somewhat analogous with the foregoing is the second of these objections, namely, the fully proved low altitude of the glaciated lands when the ice-sheets attained their maximum extent and during the diversified and fluctuating history of their recession. It must be recognized, however, that we have in the complex series of drift deposits left for our examination only a representation of the later and closing phase of the Ice age, while the land was low or near its present level. The comparatively much longer early phase of high altitude attending the accumulation and slow extension of the ice-sheets on this continent is not clearly represented by the drift and numerous moraines of the glacial retreat or of the extreme limit of glaciation, but by the earlier fluvial Lafayette formation, in which, according to Hilgard, coarse gravel from the Archæan areas near the head of the Mississippi was carried down by that stream quite to the shores of the Gulf of Mexico, attesting, as he believes, an altitude of the Upper Mississippi region at least 3,000 feet higher than now *

The wane and departure of both the North American and European ice-sheets have been marked by many stages of halt and oscillation, whereby the flora, including forest trees, and less frequently traces of the fauna, of the temperate areas

* This Journal, III, vol. xliii, pp. 389–402, 1892.

adjoining the melting and mainly receding ice were covered by its drift at the times of temporary re-advance of the ice-border. No better illustration of conditions favorable for the burial of forest beds in the drift can be imagined than those of the Malaspina glacier or ice-sheet, between Mt. St. Elias and the ocean, explored by Russell in 1890 and 1891 and found to be covered on its attenuated border with drift which supports luxuriant growing forests. Let a century of exceptional snowfall cause a thickening and re-advance of that ice-sheet, and sections of its drift exposed after the glacial recession will show a thick forest bed of chiefly or wholly temperate species. Such re-advances of the continental ice-sheets, interrupting their retreat, are known by well marked recessional moraines in both North America and Europe. Near the drift boundary in the Mississippi basin some of these glacial fluctuations have involved long stages of time, measured by years or centuries, with important though minor changes in altitude, as shown by the excellent analytic studies of Chamberlin, Salisbury, and Leverett; but farther north, as in the large region of the glacial Lake Agassiz, the withdrawal of the ice-sheet and formation of successive moraines marking slight halts and re-advances due to secular changes in temperature, humidity, and snowfall, were demonstrably very rapid, the whole duration of this glacial lake being probably only about 1,000 years.* The vicissitudes of the general glacial retreat seem to me to have been due thus chiefly to variations of snowfall, some long terms of years having much snow and prevailingly cool temperature, therefore allowing considerable glacial re-advance, while for the greater part other series of years favored rapid melting and retreat.

Under this view we may, I think, account for all the observations which have been held in America and Europe as proofs of interglacial epochs, without assuming that there was either any far re-advance of the ice-border or any epeirogenic movements attending the glacial retreat of such magnitude as to induce the fluctuations of which the forest beds and marginal moraines bear witness. Though the whole history of the wane of the ice-sheets is indeed very complex and long, as measured by our familiar historical time units, it was yet, in my opinion, geologically very brief, if compared with all preceding geologic periods and epochs. The formerly supposed necessity of predicating long interglacial epochs seems to me a misunderstanding. Instead, as Dana, Wright, Hitchcock, Lamplugh, Kendall, Falsan, Holst, Nikitin, and many other glacialists believe, the Ice age seems to me to have been essentially continuous

* Geol. and Nat. Hist. Survey of Canada, Annual Report, New series, vol. iv, for 1888-89, p. 51 E.

and single, with important fluctuations, but not of epochal significance, both during its advance and decline.

The Champlain subsidence of the land beneath its ice-sheet probably affected the whole of the preglacially elevated area before the growth of the ice-sheet was checked. For some time the increase in the ice accumulation may have exceeded the rate of depression, so that the surface of the thickening ice-sheet continued to hold an undiminished altitude. But at length the subsidence brought a warmer climate on the southern border of the ice, causing it to retreat, and probably giving to it a mainly steeper frontal gradient than during its growth and culmination. To this steeper gradient and consequently more vigorous glacial currents I attribute the larger morainic accumulations of drift marking retreatal stages than on the outermost drift boundary. When the ice had considerably receded, the outer portion of the depressed area was somewhat uplifted, to approximately its present height, which it has since held, excepting minor oscillations. Gradually, as the ice withdrew from south to north, a principally permanent wave of land elevation has followed, earliest uplifting the lœss region of the Mississippi basin, later the areas of Lake Agassiz, of the Laurentian lakes, including Lake Champlain, and of the St. Lawrence valley, and latest the country surrounding Hudson Bay, where this movement is still in progress. The time since the departure of the ice there has been too short, as in Scandinavia, to allow the earth's crust yet to have completed its restoration to an isostatic condition.

Art. XVII.—*On Antennæ and other Appendages of Triarthrus Beckii;* by W. D. Matthew.

[Read before the N. Y. Academy of Sciences, May, 1893.]

Among the problems which palæontologists have in vain tried to solve was, till a few years ago, that of the structure and affinities of the trilobite. In all the vast numbers of these animals which have been found and studied, scarcely any parts have been preserved besides the dorsal shield and hypostome. The legs, gills, and such other organs as they may have had, have practically never been shown on any specimen. This is chiefly because of the easy break afforded by the hard, smooth, carapace, but partly also because of the character of these organs, which seem to have been soft, easily disjointed, and prone to maceration and decay. The only cases, so far as I know, in which the organs of the under side have been defi-

nitely seen and described, are three specimens of *Asaphus platycephalus**—all found at different times and places—in which a number of legs are preserved in a fragmentary way, another of the same genus showing a palpus† attached to the hypostome, and a few cases in which a detached leg or antenna was found in company with species of trilobites, and referred to one of them. Other discoveries have been reported from time to time, but not conclusively verified.

It has, however, been found possible by cutting thin sections of trilobites especially well preserved, to determine the nature and position of the organs of the under side. Mr. C. D. Walcott‡ in 1881 published the results of a very successful investigation of this kind, extending over several years, and based on the study of over 2000 thin sections. His article has given us a very complete knowledge of the organization, at least of the two genera Ceraurus and Calymene, which were the subjects of his study.

The structure as thus determined involved:

1. *A ventral membrane* over the under side of the body, with hardened arches across each segment, bearing the appendages.

2. *Cephalic limbs.* There were four pairs of these, the last of which was larger and expanded at the terminal joint into a swimming organ. The bases of these limbs were manducatory in their action as in the modern King-crabs.

3. *Thoracic and abdominal appendages.* One pair of legs was found to be attached to each segment of the thorax and pygidium. On the basal joint of each was a small epipodite, and two branchiæ, which were in the form of narrow spiral ribbons. The legs, like those of the head, were generally composed of six joints, which were more or less conical, the basal end smallest. Other forms of gills were also met with, viz: a straight uncoiled ribbon in immature specimens, and a radiating leafy form found sometimes in the anterior part of the thorax. There is no mention of cephalic gills.

4. No trace of any *antennal system* was found.

Mr. Walcott concludes that the trilobites were more nearly allied to the Limulids than to any other living form, and should be classed with them and the Eurypterids, but as a separate subclass. As to their habits, he concludes that they probably were free swimming only when young, and crawled around on the bottom, with very limited swimming powers, when mature.

* Quar. Jour. Geol. Soc., 1870, p. 479; Cincinnati Jour. Nat. Hist., vol. vi, 1883.

† Quar. Jour. Geol. Soc., 1870, p. 486.

‡ Bull. No. VIII, Harvard Museum of Nat. Hist. Mr. Walcott gives very complete references and history up to that date, which I have not thought necessary to repeat.

Within the past few months Mr. W. S. Valiant has collected a very considerable number of specimens of *Triarthrus Beckii*, in which the organs of the under side are attached to the body and fairly well preserved. They occur in the Hudson River shales* near Rome, N. Y. A number of the best specimens are now in the Museum of Columbia College, and Prof. Kemp has very kindly given me the privilege of describing them.

The trilobites are found in a soft, fine, black shale and are very perfectly preserved. The most noticeable character about them is the presence of long, many jointed, rod-like attachments to the front of the head, which resemble exactly the antennæ of other crustaceans. These come out close together from just under the center of the anterior border of the headshield, and diverge generally at an angle of 30° or 40°. In one specimen (fig. 1) a length considerably exceeding that of the glabella is shown ;† in the rest they are more broken, but a considerable length is preserved in three or four, and the stumps are distinctly seen in upwards of twenty others. They curve slightly outward and taper gradually down toward the end; the tip itself is not preserved. These antennæ are composed of a great number of joints, each of which is conical, about half as long as wide, and smallest at the base. (See fig. 1*a*.) As preserved in the rock, they are calcareous, but seem to have been of a structure less firm and thick than the substance of the carapace. Their point of origin seems to be under the front part of the glabella, as they can be traced a little way under the headshield, where they almost coalesce, then turn upward and outward and disappear; with no joints in this part, so far as I have been able to follow it. (See fig. 2.) Just over the spot where they come out, the anterior margin is arched slightly upward, seemingly to give room for their play to and fro.

These organs must certainly belong to the trilobite; when attached they are in all cases in exactly the same position, and are but rarely to be seen separate; moreover, in a number of specimens in which they were not shown they were developed by cutting away the matrix in the proper place. Their character seems also tolerably certain, as both in position and structure they are like the antennæ of modern crustaceans. The appearance of the right hand antenna in fig. 3 may indicate that these organs could be bent back under the sides of the head—but this point needs more evidence. Another specimen,

* Though referred to the Hudson River by Mr. Valiant, Prof. Whitfield is disposed, on palæontological grounds, to consider them as Utica shales.

† Mr. Valiant has since shown me a specimen which has antennæ one and a half times as long as the glabella. He informs me that there are now about sixty specimens showing antennæ.

belonging to Prof. A. H. Chester, shows an antenna with the end coiled spirally inwards.

Besides these, there are shown in several of the specimens, other appendages, some of which may be branchial in their character, and others walking or swimming legs. In fig. 1 the side of the head-shield has been broken away, exposing the appendages apparently of three cephalic segments. These are of two kinds, one of which is a narrow, jointed cylindrical leg, and the other is thin, broad and leafy, with what seems to be a comb-like structure similar to the gills of many crustacea. These branchiæ, if so they be, depend from a narrow, thickened anterior edge or limb; they seem to correspond with two of the three legs shown in the specimen, and to overlie them. By analogy with Mr. Walcott's determinations, they are probably attached to the basal joint of the legs.

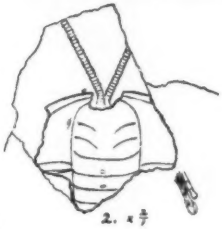
In figs. 2, 3 and 6 are shown the ends of appendages which projected from under the carapace, and seem to belong to the thoracic region. These are likewise of two kinds, one flat, furrowed, and showing a series of oblique parallel lines all along it (see figs. 2, 2*a*, 3 and 4); and the other a strong tapering leg, with three cylindrical or slightly flaring joints visible (see figs. 2, 2*a*, 3. 5 and 6). The first may be a branchial appendage; it is flattened and appears in one case to broaden out into a small paddle at the tip (though this may very likely be deceptive); it has a sharp ridge and narrow furrow along the anterior edge, and behind that the series of lines or comb-like structure, which may be due to the remains of hairs or gill structure on the limb.

Figure 4 shows a series of appendages of both kinds, but very poorly preserved. In figure 7 the projecting appendages of the tail-piece are shown, and it may be seen that apparently several, and perhaps all of the pygidial limbs are anchylosed, so as to make a rounded flap, which in shape, though not in structure, reminds one of the telson of a crayfish, and may possibly have served somewhat the same purposes.

The conclusions as to the nature of these appendages are only provisional, and may be much changed by further discoveries. They are not nearly as well preserved as the antennæ, nor in so considerable a number of specimens; for besides those figured, there are but two or three others which show them at all, and those only in traces. The shape and structure of the supposed branchiæ, in particular, are very hard to distinguish; the figures given, however, represent as far as I can see the actual outlines preserved.

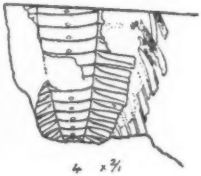
It will be seen that the structure of Triarthrus must have differed not a little from that described by Mr. Walcott in Calymene and Ceraurus. The presence of antennæ, the pecu-

1 × 2/7



2. × 2/7

1a. × 4/7

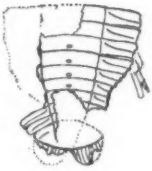


4 × 3/1

6. × 6/1

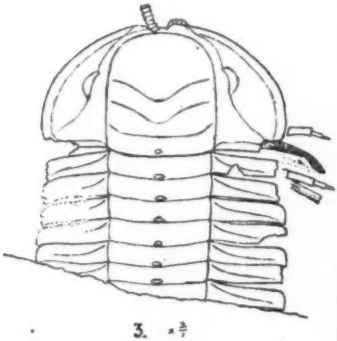
2a. × 4/7

5. × 1/1



7 × 3/1

7a. × 3/1



3. × 2/7

W & Mc

liar cephalic organs, and the anchylosed flap under the pygidium, would all be important points of difference, and indicate that the Trilobites were quite varied in structure, and probably included several widely differing types. If the classification founded on the characters of the shield is not deceptive, we may perhaps consider that the structure of Triarthrus was that of all the Olenidæ, the family to which it belongs; while many of the later trilobites would come nearer to Calymene and Ceraurus in their structure.

As regards the probable affinities of the trilobite, as modified by Mr. Valiant's discovery, the writer can scarcely venture any remarks, except tentatively. The homology with Limulus seems not to be as close in Triarthrus as in the forms studied by Mr. Walcott; but the characters seem to be of a more comprehensive type, approaching the general structure of the other Crustacea rather than that of any special form. The presence of antennæ need not, one would think, separate them from the Pœcilopoda; for a small pair occurs in Eurypterus, and the anterior pair of appendages in Limulus are thought to be modified antennæ. The cephalic organs are peculiar, if proved to be gills, and though in the solitary specimen showing them they seem to belong to the head, yet farther proof would be desirable that they are not displaced thoracic limbs. The fused pygidial flap may be a less important character, as it might be induced by some change of conditions of life.

As regards the habits of Triarthrus, we may conjecture that it usually scuttled through the soft mud which composed the shale in which it is found, on the little pointed walking legs; but that it had considerable swimming powers, more so perhaps than the later types of trilobites.

It is hardly to be expected that these antennæ, still less the other organs, will be found in specimens of trilobites unless they are exceptionally well preserved. But one character, the arching of the anterior rim at the center of the head—if not a mere accident of preservation in these specimens—may be found to exist in less perfect fossils, and would be a fair indication of the former existence of antennæ which passed under it.

In conclusion, I wish to acknowledge the kindness of Prof. Kemp in allowing me the privilege of describing these specimens. I have also to thank Prof. Whitfield for advice and assistance which have been very useful to me in the subject.

Note.—As regards the supposed gills under the head, it would seem more probable that they were long, thickly set hairs or fimbriæ on a narrow limb, and served as mouth organs rather than gills, though perhaps also assisting in the respiration.

Geological Department, Columbia College.

Art. XVIII.—*On the Reduction of Nitric Acid by Ferrous Salts;* by Charlotte F. Roberts.

[Contributions from the Kent Chemical Laboratory of Yale College—XXV.]

Among the most common methods for the estimation of nitric acid are those which depend upon its reduction by a ferrous salt in acid solution. The amount of the nitrate acted upon is reckoned either from the oxidation of this ferrous compound or from the nitric oxide set free and subsequently determined. The first named method was first put in practical form by Pelouze, and in its present modified form,* is capable of yielding accurate results in the analysis of pure nitrates. Organic matter interferes, however, with the accuracy of the indications of Pelouze's process. Schloesing† was the first to use the nitric oxide evolved as a measure of the original nitrate, and he was able to show that the presence of organic matter does not influence the yield of nitric oxide in the decomposition. Schloesing originally estimated the nitric oxide by collection over mercury, re-conversion by the action of oxygen to nitric acid, and titration of the last with standard alkali, but Reichardt,‡ Wildt and Scheibe§ and others have very much simplified the apparatus of the original process, and shown that the gas may be collected over caustic soda or potash without materially diminishing the accuracy of the analytical process. Schulze and Wulfert‖ determined by direct measurement the nitric oxide collected over mercury, and Tiemann showed that the determination loses little in exactness when the gas is measured over an aqueous solution of caustic soda.

Many modifications and extensions of these processes have appeared from time to time, the detailed consideration of which is not essential to the purpose of the present discussion, but all, whether dependent upon the determination of the change of condition of the iron salt in the residue, or upon the estimation of the nitric oxide evolved, rest upon the assumption that under the conditions of action nitric oxide is the sole reduction product in the complete destruction of the nitric acid by the ferrous salt. That this assumption is true in the main is evidenced by the analytical results of the methods. Thus, in his careful and critical examination of methods, Eder¶ found that the indications given by titration of the residue of treatment with ferrous chloride and hydrochloric acid by means of potassium permanganate showed errors of excessive oxidation amounting only to 0·3 per cent to 1 per

* Fresenius, Quant. Anal., 6th Aufl., p. 519.
† Ann. de Chemie, III, xl, 479.
‡ Zeitschr. für Anal. Chem., ix, 26.
§ Zeitschr. für Anal. Chem., xxiii, 151.
‖ Zeitschr. für Anal. Chem., ix, 400.
¶ Zeitschr. für Anal. Chem., xvi, 267.

cent upon amounts approximating 0·4 grms. of potassium nitrate, although the process involved the uncertainties of titrating, without the now used precautions, with permanganate in hydrochloric acid. The similar process in which use is made of ferrous sulphate in sulphuric acid, instead of the chloride in hydrochloric acid, gave excellent results and showed errors of loss of the nitrate ranging from 0·05 per cent to 0·4 per cent upon similar amounts of the nitrate, while Braun's process of determining the oxidized iron by stannous chloride gave upon amounts of the nitrate varying from 0·16 grms. to 0·32 grms. errors of 0·3 per cent to 1·5 per cent.

In the processes involving the treatment of the nitric oxide, the errors are usually greater and more variable. Thus, Schloesing's process gave Eder errors of 0·2 per cent to 2 per cent upon approximately 0·15 grms. of the nitrate, and 10 per cent and 12·5 per cent respectively upon 0·0279 grms. and 0·0249 grms. of the nitrate. In Reichardt's modification the errors are slightly larger on the average but vary similarly, and Tiemann's method of measuring the gas over caustic soda yields results closely comparable with those of the Reichardt process and but little inferior to those of Schloesing.

The way in which the results vary in all the processes in which the nitric oxide is estimated has very generally been regarded as suggestive of an oxidizing action upon the nitric oxide, nearly constant in amount, and productive of increasing percentage errors as the amount of nitrate decreases. The intermixture of ordinary air would naturally produce diminution of the volume of the nitric oxide, but the oxidation of this by free air of normal composition should produce no effect upon the total volume of the gas in cases where this is measured, if the oxidation goes, as is generally supposed, to the point of forming nitrous acid ; for the introduction of a given volume of oxygen (in air) means the simultaneous introduction of four volumes of nitrogen, and the single volume of oxygen is capable of causing the disappearance of exactly four volumes of nitric oxide converting it into nitrous acid, so that four volumes of nitrogen would be left to replace the four volumes of nitric oxide removed. If the oxidation be supposed to go to the point of forming some nitric acid there should be left three volumes of nitrogen to replace every volume of nitric oxide converted to nitric acid, and the total volume should be greater after oxidation than before.

In order to account for the low results, therefore, on the assumption of an oxidizing action due to free air, we must conclude that such air is derived principally from solution in the reagents, which would naturally hold oxygen in excess of the proportion in which it exists in atmospheric air. Air in solution in the receivers would most readily produce the ob-

served decrease in volume, for the nitrogen in dissolved air would naturally still remain dissolved without relation to the disappearance of dissolved oxygen. If the deficiencies observed in Schloesing's process are due at all to oxidation of the nitric oxide, it is natural to suppose that such oxidation must take place during the passage of the gas from the evolution flask to the mercurial receiver, but in the processes which involve the collection of the gas over aqueous caustic alkali oxidation might readily be brought about by dissolved oxygen, and in this case the nitric oxide removed would not be replaced by nitrogen. The last mentioned source of error, Glaser* has recently proposed to correct by collecting the gas over a solution of potassium iodide instead of over caustic soda.

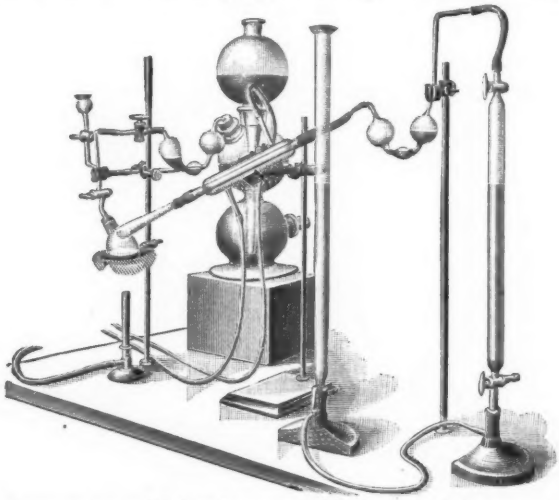
The deficiency in the total volume of gas may also be caused partially or wholly by the solubility of nitric oxide in caustic alkali. Warington† has shown that caustic soda is capable of slowly absorbing nitric oxide, and Russell and Lapraik‡ state that upon long standing over caustic soda, nitric oxide is decomposed into nitrous acid, nitrous oxide, and nitrogen.

Errors of the same sort and in the same direction as those produced by the action of caustic alkali, either alone or with dissolved air, or of air in the apparatus, would be the natural consequence of a failure of the ferrous salt to effect decomposition exactly according to the assumed reaction. Incompleteness of decomposition of the nitric acid, or the formation of an oxide of nitrogen higher than nitric oxide would result in producing too small a volume of nitric oxide, and so also would the over reduction of the nitric oxide to nitrous oxide or nitrogen. We have, moreover, abundant evidence on the one hand both of the incompleteness of decomposition of nitric acid, and of the production of a higher oxidation product by the action of the ferrous salt under modified conditions, and, on the other hand, the statement of Carius§ that prolonged contact of nitric oxide with ferrous sulphate induces further reduction of the nitric oxide. Thus, Abel and Bloxam‖ found that when the nitrate was introduced into a boiling solution of ferrous sulphate containing an excess of sulphuric acid, nitrous acid was evolved, and some nitric acid remained unaltered even after prolonged boiling; and Eder¶ after demonstrating (at least inferentially from analytical results) that practically complete decomposition to nitric oxide results when the nitrate is put into a strongly acid and cold solution of ferrous sulphate in excess, and the heating made gradual, showed that under conditions otherwise similar excepting that the mixture was *boil-*

* Zeitschr. für Anal. Chem., xxxi, 285.
‡ Journ. Chem. Soc., xxxii, 35.
‖ Journ. Chem. Soc., ix, 97.
† Journ. Chem. Soc., xxxvii, 476.
§ Ann. Chem. u. Pharm., xciv, 138.
¶ Zeitschr. für Anal. Chem., xvi, 267.

ing when the nitrate was introduced, a higher oxide of nitrogen was evolved in quantity sufficient to be visibly red, while the oxidation of the ferrous salt in the residue fell to ninety per cent of its normal value.

These facts and the consideration that the analytical methods in which the nitric oxide is estimated give without exception unexpectedly low results have led me to look a little more carefully into the conditions under which the reaction of ferrous salts upon the nitrate may be expected to give the volume of nitric oxide most nearly approaching the theoretical yield.



The apparatus which I have found most satisfactory for this work consists of a small tubulated retort, upon the neck of which is fitted a small condenser to prevent loss of liquid during the distillation. Into the tubulature of this retort is fitted tightly, by a carefully ground joint, a tube drawn out so as to dip below the surface of the liquid, and fitted with carefully ground stop-cocks,—as shown in the figure,—and so branched above as to make it possible to transmit carbon dioxide through the apparatus, or to admit any liquid without admixture of air. The condenser is joined to a Will and Varrentrapp bulb used as a trap, and this in turn is connected by thick vacuum tubing with a Hempel gas-burette. Carbon dioxide was generated in a Kipp's apparatus by action of boiled hydrochloric acid upon boiled marble, and the liquid was charged with cuprous chloride, following Warrington's device, to take up traces of dissolved oxygen. Notwithstanding all precautions, I have met with the generally recognized experience in finding that

the gas from the generator is never so pure that a hundred cubic centimeters of it will not leave a tiny bubble when shaken with a solution of caustic soda.

With the apparatus described the following experiments were made. Potassium nitrate (0·1 grm.) was introduced into the retort, generally in the dry condition, carbon dioxide was passed through the apparatus until the gas collected over sodium hydroxide left only the minute bubble which the gas from the generator alone had been found to give, and 40 cubic centimeters of a boiled solution of ferrous chloride in hydrochloric acid was admitted through the funnel tube, after shutting off the carbon dioxide and lowering the leveling tube of the Hempel burette. With the stop cocks arranged as in sketch, the liquid was then slowly heated to boiling and the process continued until the reaction of the ferrous salt upon the nitrate was apparently complete, when the carbon dioxide was again passed through the apparatus to secure complete removal of the nitric oxide, the absorption of the carbon dioxide being hastened by inclining and shaking the burette at intervals. The volume of the gas under existing barometric and thermometric conditions was noted. To discover how much of the gas collected was actually nitric oxide, I have found it best to absorb this gas by potassium permanganate. This is very easily and quickly accomplished by attaching a funnel to the Hempel burette through which a strong solution of potassium permanganate can be introduced. I have generally taken the precaution of adding water first in order to prevent the possibility of any local action between the potassium permanganate and caustic soda by means of which oxygen might be produced.

The following tables give the results of experiments performed in this way. In the first column is given the absolute volume of the gas unabsorbed by $KMnO_4$, in the second the per cent KNO_3 reckoned as if the total volume were nitric oxide, and in the third the percentage reckoned from the absorbed nitric oxide. In cases where potassium iodide was used in the Will and Varrentrapp tube to break up any higher oxides of nitrogen that might be formed, the amount of iodine thus set free is given.

In experiment (3) of Table I, the ferrous chloride was made by dissolving iron wire in boiled hydrochloric acid, and the potassium nitrate was dissolved in boiled water and added to the ferrous chloride. With this dilution, the reaction proceeded very slowly and it was found necessary to add several successive portions of hydrochloric acid before the reaction was complete, but the results as finally obtained are quite comparable with those obtained by a more rapid process.

I.

With potassium iodide in the Will and Varrentrapp tube.

	Vol. of unabsorbed gas.	Per cent from total vol.	Per cent from absorbed vol.	Iodine.
(1)	·45 cm³	99·98	98·1	·0004
(2)	·65	99·83	96·74	·0008
(3)	·45	100·3	97·6	·0004
(4)	·6	99·7	97·7	·0022

II.

With *water* in Will and Varrentrapp tube.

(1)	·6	97·76	95·	----
(2)	·6	97·76	95·2	----
(3)	·6	97·9	95·2	----
(4)	·6	97·4	94·7	----
(5)	2·43	97·3	87·	----

It will be seen by a glance at the tables that the best analytical results are obtained by the use of potassium iodide in the Will and Varrentrapp tube and calculation from the total volume of gas. The average of the results obtained above, omitting for a reason which will appear later the last experiment of the second series, may be expressed in this way :

	With KI.	With water.	Difference.
Per cent from total gas	99·95	97·7	2·25
" " nitric oxide	97·53	95·0	2·53
Diff.	2·42	2·7	

In each case there is an amount of gas equal to about 2·5 per cent of the total volume which is not nitric oxide. In whichever way reckoned the total amount of gas collected is about 2·5 per cent greater when potassium iodide is used than when water is used in the Will and Varrentrapp tube. This would indicate that some higher oxide of nitrogen is formed and is decomposed by the potassium iodide with a liberation of nitric oxide equal to about 2·5 per cent of the total volume of gas. In case the formation of this oxide were due to traces of air which oxidized the nitric oxide to nitrous acid, the volume of nitrogen thus left would be, as has been shown, exactly equal to that of the nitric oxide oxidized, and therefore there should be about 2·5 per cent of gas incapable of absorption by potassium permanganate, which is practically found to be the case. This would furnish, then, a simple explanation of the results given. Supposing this explanation to be the correct one, the presence of air should not influence the total volume of gas in case potassium iodide is not used. To test this point, the last experiment of the second series was performed. This experiment was done in exactly the same way as the others except that the carbon dioxide was not allowed to pass through long enough to displace the air completely. It will be observed that the total volume of gas is practically the same as in the

other experiments, but, as would naturally be expected, the volume of gas incapable of absorption by potassium permanganate is much increased.

An interesting confirmation of the supposition that small quantities of air introduced into nitric oxide confined over caustic soda would not influence the total volume of gas was found in some experiments performed later. After the nitric oxide in the Hempel burette had been accurately measured, air was introduced through the upper stop cock, a cubic centimeter at a time, and the burette lightly shaken. It was found that more than twenty cubic centimeters of air could be introduced in this way without materially affecting the total volume of gas, but that the volume began to increase when about one cubic centimeter of nitric oxide was left unoxidized, as subsequently determined by potassium permanganate.

In the fifth experiment of Table II, supposing the 2·43 cubic centimeters of unabsorbed gas to represent nitrogen left from air which had oxidized the nitric oxide to nitrous acid 2·5 cubic centimeters of nitric oxide would thus have been made to disappear, and the amount of nitric oxide left should be 89 per cent, 2 per cent higher than that obtained. On the same supposition, in the four preceding experiments, the ·6 cubic centimeters of unabsorbed gas represent a loss of ·6 cubic centimeters of nitric oxide which corresponds to a loss of about 3 per cent on the nitrate, so that the results reckoned from the absorbed gas should be about 97 per cent instead of 95 per cent as found. Here, again, is an unexplained loss of about 2 per cent. Moreover, with the use of potassium iodide, it is plain that, in whatever way these higher oxides of nitrogen may be formed, they should be entirely broken up into nitric oxide, so that the amount reckoned from the absorbed gas should be 100 per cent, whatever the total volume may be. We find instead that we get an average of 97·6 per cent, a loss of a little more than two per cent. It seemed probable, then, that as these experiments were done, there was a loss of from 2 to 2·5 per cent of nitric oxide by solution in caustic soda. This loss would mean the solution of ·5 to ·6 cubic centimeters of the gas after being thoroughly shaken with about 75 cubic centimeters of strong caustic soda, an amount of solubility which did not seem at all improbable and which would be quite in accordance with the results of Warington's experiments, previously mentioned.

The following set of experiments was therefore undertaken with the double object of studying the solubility of nitric oxide in caustic soda, and noting any conditions of temperature or proportions which might influence the course of the reaction. The same apparatus was used as in the preceding experiments except that a Geissler tube filled with water was inserted be-

tween the Will and Varrentrapp tube and the Hempel burette to prevent the possibility of any iodine being carried over mechanically into the gas receiver. In all cases the Will and Varrentrapp tube was filled with potassium iodide, and the amount of iodine liberated estimated by titration with sodium thiosulphate.

III.

	Per cent reckoned from total vol. of gas.	Amount of iodine in grams.
(1)	99·	·0024
(2)	100·5	·0043
(3)	99·2	·0150
(4)	99·4	·0020
(5)	100·8	·00355
(6)	98·9	·0008

In the last five experiments of this series, the caustic soda solution was thoroughly boiled to eliminate any error which might arise from oxidation of the nitric oxide by air dissolved in the liquid, but with no marked difference in the results.

In all except the last one of these experiments, the nitrate and ferrous chloride were brought together in a more or less hot solution instead of being heated gradually, and although the amounts of iodine vary, it will be seen that they are on the whole greater in this series than in the experiments in which the reacting bodies were brought together in the cold. This would indicate the possibility of some slight local action in the hot solution by which higher oxides of nitrogen are generated, but any analytical error from this source is corrected by the use of the potassium iodide which converts them into nitric oxide.

In experiment (3) of this series, where a very large amount of iodine is liberated, only one half as much ferrous chloride was used in proportion to the amount of nitrate as was taken in the other experiments, so that the amount of iron present must have been very near the theoretical limit. Here the amount of iodine would indicate the formation of a higher oxide of nitrogen, an error corrected however by the use of potassium iodide so that the percentage as calculated from the total volume of gas compares well with the results obtained in the other experiments. In experiment (6) also, a rather small excess of the $FeCl_2$ was taken (·255 grms. Fe being weighed out, whereas ·168 is theoretically required), but in this case the liquids were almost cold when brought together, and the amount of iodine set free is very small.

In several cases experiments were made to test the solubility of the nitric oxide in caustic soda. In experiment (2) the gas was allowed to stand over the liquid, with frequent shaking, for about an hour when the volume had decreased from

24·8 to 22·6 cubic centimeters. In experiment (3), after the lapse of an hour with similar treatment, the volume of gas had decreased four cubic centimeters, and one cubic centimeter was lost by the gas simply standing over night over caustic soda.

To determine whether the nitric oxide went into solution as such or in the form of nitrite, the following experiments were performed. About 30 cubic centimeters of the liquid were drawn off by stopcock at bottom of Hempel's burette into an acidified solution of potassium iodide, freely exposed to air, and the amount of iodine set free determined by titration with sodium thiosulphate. Again, 30 cubic centimeters more of the same solution were treated in exactly the same way except that the flask containing the potassium iodide was first filled up with carbon dioxide and air carefully excluded. On two trials it was found that the amount of iodine set free under the latter circumstances was very small, and less than one-half as much as that set free when air was admitted freely, showing very plainly that some, and perhaps most, of the nitric oxide was dissolved as such, without chemical action of the caustic soda.

The principal conclusions to which this study of the estimation of nitrates, by measurement of the volume of nitric oxide swept along by carbon dioxide and collected over caustic soda, has led me, are as follows:

1. The best analytical results are obtained according to this method by passing the gas through potassium iodide before collection, and estimating from the total volume of gas collected.*

2. If air be present in the apparatus at the outset, it will not affect the total volume of gas if potassium iodide be not used, or if the nitric oxide meet the air beyond the Will and Varrentrapp bulb. When potassium iodide is used, air in the apparatus would make the total volume too large, but with small amounts of air, this error is counterbalanced by the solubility of nitric oxide in caustic soda.

3. Since the nitric oxide is perceptibly soluble in caustic soda upon shaking, the gas should not be left long in contact with the liquid before the volume is measured.

4. If the hydrochloric acid used is very dilute, the reaction proceeds very slowly, but leads finally to the same results.

5. If the nitrate and ferrous salts are brought together hot, some higher oxides of nitrogen may be formed, but the error is corrected by the use of potassium iodide.

6. If potassium iodide is used the results are accurate even when the ferrous chloride is present only in very slight excess.

* This result accords with Glaser's experience in collecting the gases evolved unmixed with CO_2, over KI—[loc. cit.]

Art. XIX.—*Concerning the Structure of Caoutchouc;* by Hermann F. Lueders.*

While examining a number of specimens of crude rubber from various regions, with regard to their impurities, my attention was directed to the microscopic characters of the rubber itself. The literature on the subject being scanty, it appeared as if a brief examination of the matter might be profitable. The following is a short summary of my results.

Being unable to procure fresh stems of any rubber-producing plant, except *Ficus elastica*, the succeeding details concerning the appearance and properties of the latex are taken from that plant only.

In *Ficus elastica* the caoutchouc is found in the copious latex which is contained in relatively narrow, branching vessels, abundant in the hypodermal and pith parenchyma. The caoutchouc exists in the form of small, colorless globules on the average 3μ in diameter; collected under oil of almonds it retains the original appearance for some time; in about half an hour the globules begin to coalesce, while at the same time, solid particles separate out of the menstruum in which the droplets are suspended. If the latex exudes in the air, the coalescence of the globules is very rapid and, with the evaporation of the watery material, results in the speedy formation of a transparent film, soluble in chloroform, ether, benzole, carbon disulphide and similar solvents.

There remains, however, an abundant white residue when the dried latex is treated with any of the above solvents. This residue consists of acicular or tabular crystals and grains. Its behavior in presence of acids and other reagents, before and after ignition, seems to indicate its identity with calcium oxalate, while traces of starch are also found to be present.

Faraday† found that a specimen of latex, brought in a sealed bottle from South America, had an acid odor. It does not appear from what plant the latex in question was derived, nor whether its acidity was original or due to fermentation. In *Ficus* the latex shows a weak alkaline reaction brought out only by delicate indicators. The coalescence of the caoutchouc globules under the influence of the air takes place quite rapidly and completely so that the solidified latex rarely shows any globules, nor have any of the specimens of crude rubber in the Harvard Botanical Museum, which I had the privilege

* Presented to the American Academy of Arts and Sciences, Boston, by Professor Goodale.

† Quar. Jour. of Science, Literature and the Arts, xi, p. 15, quoted by Wiesner.

of examining, shown the presence of rubber globules still distinct in the mass, although Wiesner* states that he distinguished them in one variety.

But even if solidification obliterates all traces of the original globules, does not the rubber in its solid state show a structural arrangement common to all its varieties?

Payen† claims for it an irregular reticulated structure, Wiesner‡ finds also many cases of reticulation, though also some where only a crumpled foliar structure was visible. Faraday on the other hand regards rubber as structureless. Of the twenty specimens which I examined no two agreed in their microscopic structure; three main types might, however, be distinguished. Namely (1) the blistery flowage (2), the reticulated, and (3) the stratified. Reticulation proves of infrequent occurrence, while stratification predominates. The coarse stratification can generally be shown to be parallel to the surface of the rubber mass, while solidifying. Most stratified specimens showed a system of crumpled, branching, or broken crosslines, such as might be formed by the shrinking of any drying layer. In some of the stratified specimens, peculiar illusory appearances are discernible resembling roughly the structure of wood-cells of certain conifers or in a few cases ducts of angiosperms. These misleading appearances are produced by particles of included dust, fragments of wood bark, and the like.

Different parts of the same sample are frequently found to possess unlike structure. These facts lead us to doubt not only the presence of a definite structure common to all kinds of rubber, but also of any structure distinctively peculiar to each one.

In order to place the above statement on a yet firmer basis I made chloroform solutions of various varieties of rubber. These were allowed to solidify and then sectioned and examined. Various markings were found, but none similar to those of the respective varieties before dissolving.

Caoutchouc then has no definite structure, *per se*, and all apparent structure is only the result of the conditions under which its coagulation from the latex, and subsequent solidification take place.

In Wiesner's discussion of the microscopic properties of rubber, occur the following statements: "all varieties of rubber so far as examined by me, appeared, between the Nicols of the polarizing microscope, in brilliant colors." "The polarization colors appear most striking if a thin section of caoutchouc is strongly compressed between two slides."§

* Wiesner. Rohstoffe des Pflanzenreiches, p. 158. † Compt. Rendus, xxxiv.
‡ Rohstoffe, p. 164. § Rohstoffe, pp. 164, 165.

The latter statement suggested the question, whether the colors so observed, might not be merely the result of tension which must here undoubtedly exist in consequence of the pressure.

All samples on hand were examined with reference to this property. Thin sections were made with a razor, and placed without a coverglass on the stage of a polarizing microscope; every one of them displayed colors more or less striking.

Then arose the next question: the tension of pressure had indeed been obviated in the last series of tests, but might not the mechanical operation of cutting produce a tension on the surface of the adhesive rubber?

To answer this, several tests seemed applicable. By washing a section in chloroform, the superficial layer that might have been stretched in cutting could be removed. By cutting a section with a hot platinum wire, tension was not likely to be produced. By dissolving and then drying rubber it could be examined before any outside force, other than surface tension, could have influenced it. By examining fresh latex, liquid or dried, the properties of the original globules could be ascertained. The results of these different tests agree completely; no colors appear. When, however, the resolidified rubber or dried latex was sectioned however carefully or quickly, or stretched, colors invariably appeared. These results, and absence of polarization-colors whenever tension was removed, presence of colors where tension might exist, allow but one conclusion. The property of displaying various prismatic colors under the rotating Nicol of the polarizing microscope, probably does not belong *as such* to any of the varieties of crude rubber brought into our markets, and these colors so frequently noted are best explained as incidental results of the way in which the objects are generally prepared for examination.

ART. XX.—*Fisher's New Hypothesis;* by GEO. F. BECKER.

IN the June number of this Journal* Mr. O. Fisher reaches the conclusion that on an earth of small viscosity, that is a fluid globe, the height of the oceanic tides would be diminished by only a moderate fraction of its height on a rigid earth. He infers that the existence of tides of short period does not indicate a high value for the rigidity of the earth; a conclusion of great interest to geologists, some of whom per-

* Vol. xlv, p. 464. 1893.

haps will not care to undertake an examination of the reasoning employed in reaching it.

Mr. Fisher obtains this unlooked for result by discussion of a formula of Prof. G. H. Darwin giving the height of the oceanic tide relatively to the nucleus on the "canal theory" for a yielding earth, whether the yielding is elastic or not. For comparison Darwin also states the height of the relative tide on the equilibrium theory for the same value of the potential.* The formulas involve the lag of the tide, which disappears when the case of a fluid earth or that of a rigid earth is considered.

Neglecting the lag, the formula for the "canal theory" may be written

$$a_n - r = \mathrm{R}\left(1 - 2\mathrm{A}\,.\,\frac{2g}{5\tau}\right)$$

where r is the radius of the tidal water-surface, a_n the radius of the nucleus, R one-half the total amplitude of the tide on a rigid earth, g the acceleration of gravity, A (which Darwin denotes by E) the greatest semi-amplitude of the bodily tide at the equator and τ is three times the moon's mass into the square of the earth's mean equatorial radius divided by twice the cube of the moon's distance.

The formula for the equilibrium theory under the same conditions is

$$r' - a'_n = \mathrm{R}'\left(1 - 2\mathrm{A}\,.\,\frac{2g}{5\tau}\right)$$

where the primed letters denote quantities corresponding to the same letters unprimed in the other formula.

From a comparison of the full formulas, equally applicable to those given above, Darwin points out that where the one formula gives high water the other gives low water. This is also the main difference between the theories.† Either formula gives the tide on a rigid nucleus when A is zero. For a fluid homogeneous globe A is the same on either theory.

Mr. Fisher draws his own conclusions from an evaluation of $2\mathrm{A}\,.\,2g/5\tau$, which he computes at 2/5 nearly. He infers that on the canal theory the tides cannot be less than 3/5 of their height on a solid globe.‡ He might also by the same

* Phil. Trans., vol. clxx. p. 26, 1879.

† Compare Darwin's article on tides, Enc. Brit., 9th edition, vol. xxiii. p. 354, "tides inverted." The dynamical theory for an earth completely covered by the ocean would give tides of the same height as the equilibrium theory, if the ocean were 3.000 fathoms deep at the equator and shoaled towards the poles. In general its height depends on the distribution of depth. Ibid. section 15.

‡ Proc. Cambridge Phil. Soc., vol. vii, 1892, p. 337.

process have concluded that the tides would show a corresponding amplitude on the equilibrium theory, as appears from the formulas stated above.

Mr. Fisher's computation is incorrect because he takes for A the value which it would have for a fluid globe, homogeneous or not, were there no mutual attraction between the fluid particles. It was for the purpose of dealing with the effect of this mutual attraction that the method of "spherical harmonics" was evolved. The effect in the case of a fluid globe of uniform density throughout on the equilibrium theory, is well known to be an increase in the ellipticity in the ratio 1 to 1–3/5. The ellipticity, e, of the equilibrium lunar tide, in a fluid earth, with this distribution of density, composed of mutually attracting particles is

$$e = \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{a^3 \mathrm{M}}{\mathrm{D}^3 \mathrm{E}},$$

where (as in Thomson and Tait, Nat. Phil.) a is the earth's mean equatorial radius, D the moon's distance, E the earth's mass, and M the moon's mass.*

Since the ellipticity is small, it is easy to see that $2\mathrm{A} = ae$ and therefore also, since for this case $\mathrm{E}/a^2 = g$, substitution for A and τ of the values assigned to them above gives

$$2\mathrm{A} \cdot \frac{2g}{5\tau} = \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{a^4 \mathrm{M}}{\mathrm{D}^3 \mathrm{E}} \cdot \frac{2}{5} \cdot \frac{\mathrm{E}}{a^2} \cdot \frac{2}{3} \cdot \frac{\mathrm{D}^3}{\mathrm{M}a^3};$$

and here the second member reduces to unity by cancellation. In general, therefore, or irrespective of the fluidity of the earth, the quantity $2\mathrm{A} \cdot 2g/5\tau$ is simply the ratio of the greatest bodily equatorial tide in any special case to the equilibrium tide on a fluid earth. Thus for a fluid earth the canal theory and the equilibrium theory give the same result, viz: no relative tide, or

$$1 - 2\mathrm{A} \cdot 2g/5\tau = 0.$$

On any theory yet propounded for the tides, the existence of semi-diurnal tides indicates an earth presenting great resistance to deformation. This resistance, so far as the tides are concerned, may be due either to rigidity or to the viscosity of an ultraviscous fluid, some 20,000 times as viscous as hard brittle pitch at 34° F. In the same paper by Darwin quoted above, he comes to the conclusion "that no very considerable portion of the interior of the earth can even distantly approach the fluid state."

Washington, D. C., June, 1893.

* Compare Nat. Phil., section 819.

ART. XXI.—*Criticism of Mr. Fisher's Remarks on Rock Fusion;* by CARL BARUS.

ALTHOUGH the experiments of Profs. Roberts-Austen and Rücker* were made in answer to a query of Mr. Fisher's, I think he is laboring under a misapprehension as to their work. These gentlemen nowhere state that the rock was fused below 920°. What they do state is, "There is a large absorption of heat in the neighborhood of 800°, which raises the mean specific heat between 750° and 880° C., to the large value 0·636;" and in an earlier paragraph, "frequent heatings and coolings, and the nature of the flame—whether oxydizing or reducing—employed to heat the mass appeared to affect the results very seriously."

As the paper of Roberts-Austen and Rücker appeared about the time when I was making the diabase experiments, I looked forward to these anomalies (as I believed them to be) with interest—more particularly as Mr. King and I were on the lookout for polymerizations accompanied as they usually are with marked volume changes. But my results showed such commonplace smoothness throughout the stated interval of temperature that I gave up the chase. If, however, these anomalies are now to be interpreted as fusion, it is well to bear in mind that the melting point of silver is at about 954°; and that if dolerite melts even below 920° (750° to 880° as given above) it ought actually to run on a surface of boiling zinc.

We did not try dolerite. True we had a list of rocks to put through the mill after it had been invented;—but Congress in its wisdom saw no public value in our lucubrations and our efforts (with much else on our program) were foredoomed. It is with mingled feelings that one apologizes for one's toddling paces when there was good will enough for a journey!

However, to believe that dolerite can be slagged in a zinc pot or even fused in a candle flame is an exertion, and one is at liberty to ask the privilege of trying it.

Suppose for the sake of argument, that an absolute temperature 920°+273° is inserted into Clausen's equation instead of 1170°+273°. The effect would be to change the accepted relation of the increments melting point and pressure from

* Roberts-Austen and Rücker, Phil. Mag., xxxii, p. 353, 1891. With regard to these experiments I have already expressed myself in Phil. Mag., xxxv, pp. 296, 305, 1893. The authors themselves state "As we have not definitely proved what is the cause of these discrepancies" (those of the above text being meant), "we publish our conclusions with a certain amount of reserve."

0·025 to 0·021; but this would not materially alter the diagrams, remembering that the other constants of the equations are found independently.

As to the latent heat of fusion, it is a question whether there is such a datum strictly speaking. What I did was to idealize the case, by slightly prolonging the rate at which liquid thermal capacity changes with temperature in the direction of lower temperatures and the rate at which solid thermal capacity changes with temperature in the direction of higher temperature. The admissibility of such a process is a question of experiment; and experiment sustains it because the two loci very nearly overlap. Thus one can state that if diabase fused at such a temperature its latent heat would be so and so. The temperature to be taken is clearly the melting point obtained in the volume work.

Now, as Mr. Fisher will acknowledge, mere statements of melting point and latent heat for dolerite are inadequate, so long as the volume changes at fusion are missing. He might have made a much more startling statement by comparing diabase and naphthalene, for instance; the latter has a latent heat say twice as great as the former, in spite of the fact that diabase melts at a temperature enormously high as compared with the other body. In all this there is nothing implied either with reference to the law of fusion in question or the isometrics.

In the case of diabase, granting merely that the volume changes experimentally observed are correct, the following mean values* hold good:

Melting point	1200° C.,	$d\mathrm{T}/dp$ =	·020
" "	1100 C.,	$d\mathrm{T}/dp$	·027
" "	1000 C.,	$d\mathrm{T}/dp$	·049

To go below this it would be necessary to actually work out the relation of thermal capacity to temperature for liquid diabase. Nevertheless the data given are sufficient to show, that the lower melting point for which Mr. Fisher is angling would only accentuate our cardinal result, viz: that the rate at which melting point increases with pressure is about the same in silicates and in organic compounds. My conviction of the essential correctness of Mr. King's constructions is therefore unshaken.

* T being the absolute melting point at the pressure p in atmosphere.

ART. XXII.—*Larval forms of Trilobites from the Lower Helderberg group;* by C. E. BEECHER. (With Plate II.)

ATTENTION has previously been called to the abundance and perfection of fossils in the siliceous limestones of the Lower Helderberg group, from a limited locality in the Helderberg Mountains, south of Albany, New York. Proper methods of collecting and preparation yield quantities of the most delicate and exquisitely preserved animal remains, consisting chiefly of bryozoa, with numerous brachiopods, ostracodes, spicules of sponges, small corals, lamellibranchs, gastropods, and disarticulated trilobites. Remains of hydrozoa, echinodermata, annelids, pteropods, and cephalopods, are less frequent.

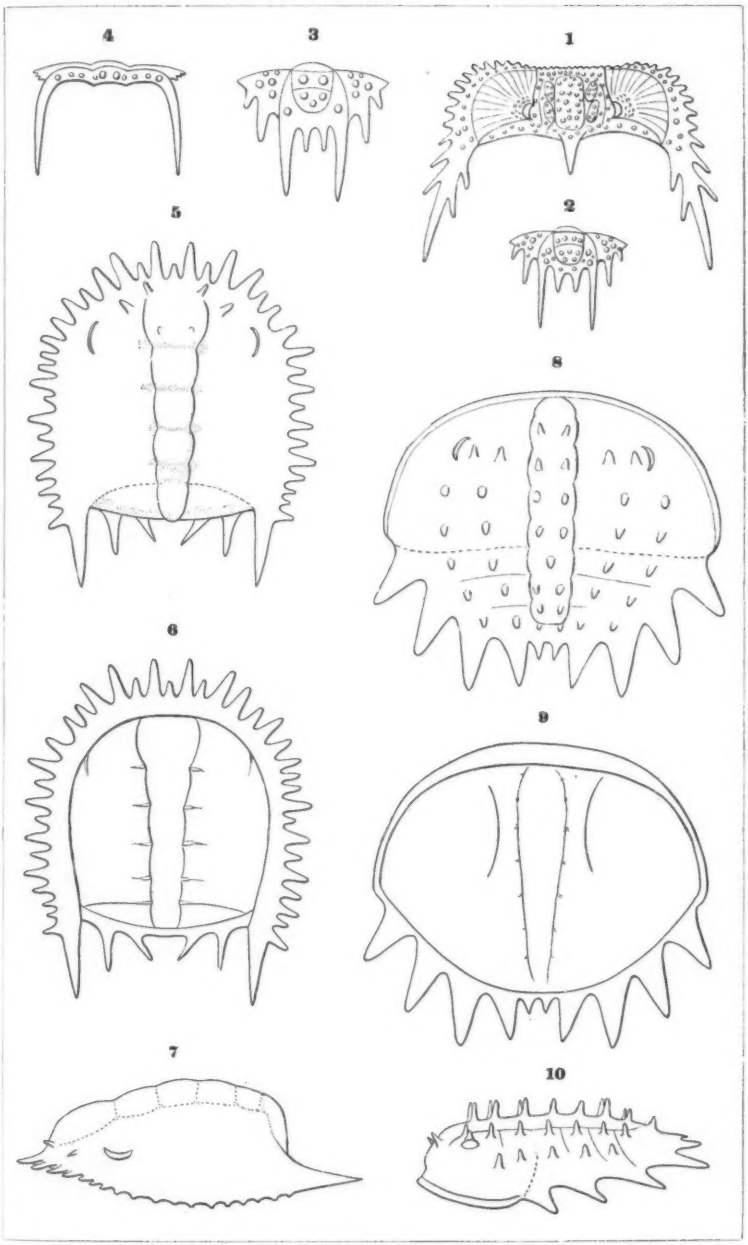
The conditions of preservation are such that not only are the large and strong species preserved, but also the smallest, and the young of many in all stages of growth. As would naturally be inferred, the study of this fauna, based upon such complete material, has brought to light many undescribed species, and has increased the range of known genera, besides affording several genera new to science. Altogether about seventy new species are now known to the writer.

Among the rarities discovered are the specimens here noticed, consisting of five larval trilobites referred to the genera *Acidaspis* and *Phaëthonides*. They represent early stages of these genera when the animals had no thoracic segments, and when the separation between the cephalon and pygidium was not distinctly marked.

Notwithstanding the abundance of trilobites in the Paleozoic rocks, and the care with which they have been studied and collected, but few are known in the early adolescent state, and extremely few in the still earlier larval stages. This paucity of larval specimens seems to be due chiefly to the sediments, which, in general, have not been favorable for the preservation of such organisms. Heretofore, the best material has come from fine shales and slates representing original muds. The most complete developmental series known are the classic ones of Barrande,* representing *Aeglina*, *Agnostus*, *Arethusina*, *Arionellus*, *Dalmanites*, *Hydrocephalus*, *Sao*, and *Trinucleus*, of which *Agnostus*, *Dalmanites*, *Hydrocephalus* (= *Paradoxides*), *Sao*, and *Trinucleus*, were observed in their larval stages.†

* Système Silurien de la Bohême, i, 1852.

† *Hydrocephalus* appears to be the young of *Paradoxides*. See Barrande, *l. c.*, and compare *Hydrocephalus carens*, Pl. 49, *H. saturnoides*, Pl. 49, with *Paradoxides inflatus*, Pl. 13, figs. 16, 17, 18, and *P. spinosus*, Pl. 12, figs. 5, 6, 7


4
3
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10

The first American larval trilobites were discovered and described by S. W. Ford.* They were specimens of *Elliptocephala* (*Olenellus*) *asaphoides* Emmons, from near Troy, N. Y., and together with the larvæ of *Sao hirsuta* were the most elementary forms known.

Next, C. D. Walcott, in 1879,† published a fine series illustrating the metamorphoses of *Triarthrus Becki* Green, from the Utica Slate. All the stages were shown, from an individual with one thoracic segment to mature specimens having thirteen to sixteen segments.

G. F. Matthew, in 1887 and 1889,‡ carefully described and illustrated embryonic and immature forms of *Ptychoparia Linnarssoni* Brögger, *Liostracus ouangondianus* Hartt, and *Solenopleura Robbi* Hartt, from the slates at St. John, New Brunswick. The youngest forms were quite as primitive as the *Sao* of Barrande and *Elliptocephala* of Ford, so that the larvæ of at least five genera have been described, representing the same early stage.

The orders of development recognized by Barrande are:

		Types.
I.	Head predominating, incomplete. Thorax nothing or rudimentary. Pygidium nothing.	*Sao hirsuta.*
II.	Head distinct, incomplete. Thorax nothing. Pygidium distinct, incomplete.	*Trinucleus ornatus* and all *Agnostus.*
III.	Head complete. Thorax distinct, incomplete. Pygidium distinct, incomplete.	*Arethusina Koninckı.*
IV.	Head complete. Thorax complete. Pygidium distinct, incomplete.	*Dalmanites Hausmanni.*

The third and fourth orders are probably later stages of the first and second, and it now seems that the second order will be found to have an earlier stage equivalent in structure to the first.

The larvæ noticed in the present paper are of peculiar interest on account of their belonging to highly ornamented and specialized genera. Moreover, some deductions can now be made concerning the permanence and uniformity of the stages of metamorphoses, as well as the acceleration of specific characters so that they appear in the larval state.

* This Journal, vol. xiii, p. 265, 1877.

† Transactions of the Albany Institute, vol. x.

‡ Illustrations of the Fauna of the St. John Group, No. IV, Trans. Roy. Soc. Canada, 1887. Sur le Développment des premiers Trilobites, An. Soc. Roy. Macol. Belgique, xxiii, 1889.

A larval form of Acidaspis.

Two species of the family Acidaspidæ are known from the rocks of the Lower Helderberg group in New York, *Acidaspis tuberculatus* Conrad, and *Dicranurus hamatus* of the same author. Both are so different that the larva figured on Plate II, figures 5, 6, 7, can be referred to the first without hesitation, since it retains one of the most characteristic features, viz: the denticulate cephalic border.

Three individuals of *Acidaspis tuberculatus* have been found in the same early stage of development. The length of the best specimen exclusive of the spines is ·93^{mm}; width ·88^{mm}. The total length is 1·3^{mm}.

The general outline is longitudinally semi-ovate, regularly rounded in front, and truncate behind; greatest width across the anterior third. Lateral and anterior margins bearing about thirty-five alternating spines or denticulations. Each posterior lateral angle is produced into a strong spine, and between them on the margin are four smaller ones. Upper or dorsal surface convex, highest posterior to the mid-length, and abruptly bent down or truncate behind.

All but the posterior truncate portion is believed to be homologous with the cephalon of an adult form, so that the posterior angles are really the genal angles. The axis is defined, convex, narrow, widest in front, and apparently divided into six annulations or lobes. The posterior one doubtless represents the axis of the pygidium, since it is limited by a furrow extending to the bases of the genal spines. The next anterior lobe would then correspond to the occipital ring, and the others to the lobes of the glabella. Two lunate prominences on each side of the axis in front are the palpebral lobes and the eyes.

On the ventral side, Plate II, figure 6, the edge of the cephalon is extended inwards, making a continuous doublure. The axial depression extends the entire length of the animal, and is divided into lobes or annulations by transverse ridges, which represent muscular fulcra and points for the attachment of appendages.

A larval form of Phaëthonides.

The larva figured on Plate II, figures 8, 9, 10, cannot at present be referred to a particular species. Only two species of *Phaëthonides* have yet been described from the Lower Helderberg, but from additional material it is now evident that other species occur in these rocks. Moreover, if this larva retains its specific characters as strongly as *Cyphaspis tuberculatus*, it cannot be referred to either *Phaëthonides*

cyclurus Hall, nor to *P. macrobius* Billings, sp., as it has a strongly denticulate posterior border, a character not possessed by either of the described species. The generic reference can be determined with more certainty, for the combination of features in the cephalic and pygidial regions cannot well exist in any genus except *Phaëthonides* found associated with this larva.

The outline is broadly elliptical transversely, and obtusely angular at the genal extremities. The cephalic portion is semi-elliptical, and includes more than half the animal. It has a narrow, flattened, entire border, and is defined posteriorly by the obtuse points, which are correlated with the genal angles. Palpebral lobes prominent, and, as in the larva of *Acidaspis*, situated nearer to the anterior margin than to the frontal lobe of the axis.

The pygidial portion is depressed convex, with five pairs of symmetrically disposed marginal denticulations or spines, of which the median pair is short.

Axis narrow, extending nearly the entire length of the animal, obscurely annulated by six or seven (possibly eight) slight constrictions. The anterior five seem to pertain to the cephalon and the others to the pygidium. The annulations each carry a single pair of spines, with the exception of one at the junction of the cephalon and pygidium, which apparently has but a single spine.

The pleural and lateral facial areas also bear double rows of spines, the anterior pairs being between the eyes and axis. The distinction between the cephalon and pygidium is very obscure, but the apparent large size of the latter in *Phaëthonides* may indicate a moult later than the first. The ventral side, figure 9, shows a narrow doublure and the axial cavity. Greatest length, 1·15^{mm}; greatest width, 1·34^{mm}.

Observations.

Many correlations have been drawn between the Trilobita and other Arthropoda, by Packard, Dohrn, Lang, and others. The present state of opinion is well expressed by Lang,* who concludes that the Trilobites are related to the Crustacea. In support of this is "the fact that the trunk feet are biramose and carry epipodial appendages." The important discovery by Mr. W. S. Valiant, of organs which can be homologized with antennæ, as announced by Mr. W. D. Matthew,† estab-

* Text Book of Comparative Anatomy, English edition, p. 415, 1891.

† On Antennæ and other Appendages of Triarthrus Beckii, by W. D. Matthew, read before the N. Y. Acad. of Sci., May, 1893. The first specimen preserving the antennæ was discovered by Mr. W. S. Valiant several years since. Recently Mr. Valiant and Mr. M. Sid. Mitchell have obtained other specimens showing more completely the nature of the appendages.

lishes the comparisons made by Lang, so that the five cephalic limbs of Trilobites would correspond "to the 5 typical limbs of the Crustacean head, and the Trilobites might then be regarded as original *Entomostraca*, to be derived from the same racial form as the *Phyllopoda*" (Lang). Also, the phylogeny and relations of *Eurypterus*, *Limulus*, and the Trilobites, are with the Crustacean radicle. The information now at hand admits of still further conclusions regarding the affinities of the *Trilobita*.

The larvæ of *Acidaspis* and *Phaëthonides*, together with those of *Sao*, *Elliptocephala*, and *Ptychoparia*, indicate that *Agnostus* is neither the phylo-typembryo nor the phylo-phylembryo, but is really the adult equivalent to an early segmented stage of the higher genera. The characters of the youngest larvæ expressed in the non-differentiation of the cephalon and pygidium, the preponderance of the cephalon, carrying at this time all the appendages, some of which are the antennæ, are strong indications of the likeness of this stage to the Nauplius or Meta-nauplius of true Crustacea. No ocelli are known, however. The early segmented stages must have resembled, more or less, such late larval Crustacean forms as the larva of *Bopryus*, one of the Isopoda, and, as suggested by Woodward and Edwards, the Trilobita may be considered as ancient or proto-isopods.

The fact that most of the smallest larvæ observed belong to the first order of Barrande, and that the second and succeeding orders represent, more or less closely, stages of development of an individual from the first, is strong evidence that the first order, or the unsegmented condition, with dominant cephalon and undefined pygidium, is the primitive stage. It is therefore probable that, with more complete material, the young of *Trinucleus*, *Agnostus* (= types of 2d order), *Arethusina Konincki* (= 3d order), *Dalmanites Hausmanni*, *Proëtus*, etc. (= 4th order), will be found to have a first larval stage like *Sao*, *Ptychoparia*, and *Acidaspis*, thus bringing all into perfect accord.

Upon this basis, the following classification of the stages of development is suggested:

Nauplius ?	Cephalon predominating, other parts not separated from it. Examples: earliest known stage of *Sao*, *Ptychoparia*, and *Acidaspis*.
Phylembryonic	Cephalon distinct. Thorax nothing. Pygidium distinct. Examples: 2d stage of *Sao*, etc., and Barrande's larvæ of *Agnostus* and *Trinucleus*.

Nepionic (As many stages as normal thoracic segments.)	Cephalon distinct. Thorax incomplete. Pygidium distinct. Examples: *Agnostus*, *Microdiscus*, and young of all trilobites lacking full number of thoracic segments.
Neanic	Cephalon distinct, complete. Thorax distinct, complete. Pygidium distinct, complete. Growth incomplete.
Ephebic	All parts complete, and full size attained.

It is interesting to note that while neither the larvæ of *Acidaspis* nor *Phaëthonides* possess the characteristic generic features of sutures and glabellar lobation, yet their specific facies is quite pronounced. The larval *Acidaspis* does not suggest *Acidaspis* nor *Ceratocephala* in general; as *Ceratocephala Verneuili* Barr., *Solenopeltis Buchi* Barr., *Dicranurus hamatus* Con., or *Ancyropyge Romingeri* Hall, but has manifest likenesses to its own species, *Acidaspis tuberculatus*, and other closely allied forms, as *A. Brighti* Murchison, *A. Hoernesi* Barr. and also several species of *Odontopleura*, which in their adult form resemble the species of *Acidaspis* in every way except in the absence of the occipital spine.

Yale Museum, New Haven, Conn., June 10th, 1893.

EXPLANATION OF PLATE II.

Acidaspis tuberculatus Con.

FIGURE 1.—Cephalon of an adult specimen. × 2.
FIGURE 2.—Pygidium of a mature individual. × 2.
FIGURE 3.—Pygidium of an immature individual. × 5.
FIGURE 4.—Segment of thorax; showing spines and ornamentation. × 2.
FIGURE 5.—Dorsal view of larva. × 38.
FIGURE 6.—The same; ventral view. × 38.
FIGURE 7.—The same; profile, slightly oblique. × 38.
Lower Helderberg group, Albany Co, N. Y.

Phaëthonides, sp.

FIGURE 8.—Dorsal view of larva. × 38.
FIGURE 9.—The same; ventral view. × 38.
FIGURE 10.—The same: profile, slightly oblique. × 38.
Lower Helderberg group, Albany Co., N. Y.

SCIENTIFIC INTELLIGENCE.

I. PHYSICS.

1. *Flame Spectra at High Temperatures. Part I. Oxy-hydrogen Blowpipe Spectra*, by W. N. HARTLEY. (Abstract, received from the author, of a paper presented to the Royal Society, May 10, 1893.)—Brewster, in 1842, first examined the spectra of salts with a flame of oxygen and coal-gas (Proc. Roy. Soc. Edinb., vol. vi, p. 145). Professor Norman Lockyer has given us maps of twenty-two metallic spectra at the temperature of the oxygen and coal-gas flame. The region observed lies between λ 7000 and 4000.

Preparatory to undertaking the study of spectroscopic phenomena connected with the Bessemer "blow" and the manufacture of steel generally, I have carefully observed the spectra of metals and metallic oxides obtained by submitting the substances to the oxyhydrogen flame.

Method of Investigation.—The method of obtaining spectra with flames at high temperatures is the following: Hydrogen proceeding from a large lead generator is burnt in a blowpipe with compressed oxygen. The blowpipe measures 3 inches in length by $\frac{3}{8}$ inch external diameter. The substances examined are supported in the flame on small plates of cyanite about 2 inches in length, $\frac{1}{20}$ inch in thickness, and $\frac{1}{4}$ inch in width. This mineral, which is found in masses in Co. Donegal, contains 96 per cent of aluminium silicate, and is practically infusible. The spectra were all photographed with the instrument employed by me on former occasions for photographing ultra-violet spectra, illustrations of which were published in the Chem. Soc. Journ., vol. xli, p. 91, 1882. The dispersion of the instrument was that of one quartz prism of 60°.

Isochromatic plates developed with hydroquinone were largely used. Various dyes for sensitizing and all kinds of developing substances were tried. The spectra were measured with an ivory scale divided into hundredths of an inch, and directly applied to the photographs, the division 20 on the scale being made to coincide with the yellow sodium line which appears in every photograph. It was found convenient to record the measurements on a gelatino-bromide paper print taken from an enlarged negative. Sometimes, for more careful and minute reference, it was found convenient to make an enlargement of the spectrum with the scale in position, but accurate measurement cannot be made in this way. It is necessary to use a low magnifying power and cross-wires in the eye-piece.

For the identification of lines already known nothing more complicated is required, but to measure new lines and bands it was considered desirable to make use of a micrometer and microscope; the screw of the micrometer was cut with 100 threads

to the inch, and the magnifying power generally used was 10 diameters.

Characters and Extent of the Spectra observed.—Just as in the ordinary use of the spectroscope we must be prepared to see the lines of sodium, and in hydrocarbon flames the bands of carbon, so in these spectra the sodium lines and the strongest lines belonging to the emission spectrum of water vapor are also always present.

In addition, the cyanite yields the red line of lithium, which is no inconvenience, but a positive advantage, serving as it does, to indicate where the spectra commence.

A large majority of the metals and their compounds all terminate somewhere about the strongest series of water vapor lines. Typical non-metallic spectra are sulphur, selenium, and tellurium; the first yields a continuous spectrum with a series of beautiful fluted bands; the second a series of fine bands, occurring at closer intervals; the third is characterized by bands still closer together and near the more refrangible termination of which four lines occurring in Hartley and Adeney's spark spectrum of tellurium are visible. Increase in atomic mass causes shorter periods of recurrence of bands. In line spectra it is the reverse; increase in atomic mass causes greater periods in the recurrence of lines. Charcoal and carbon monoxide yield chiefly continuous spectra; the latter, however, exhibits some carbon lines. The hydrocarbons yield the well-known spectrum of carbon bands with also those attributed to cyanogen. Of metallic elements, nickel, chromium, and cobalt yield purely line spectra; antimony, bismuth, silver, tin, lead, and gold beautiful banded spectra (spectra of the first order) accompanied by some few lines. The spectra are finer than those of selenium and tellurium.

Iron and copper exhibit lines, and, less prominently, bands. Manganese has a beautiful series of bands and a group of three very closely adjacent lines. Aluminium gives a fine continuous spectrum with three lines, origin uncertain, zinc a continuous spectrum without lines, and cadmium a spectrum consisting of one single line only, λ 3260·2.

Of compounds, chromic trioxide yields a continuous spectrum with six lines belonging to the metal, copper oxide a fine band spectrum with two lines of the metal, magnesium sulphate gives a spectrum of magnesium oxide consisting of broad degraded bands composed of closely adjacent fine lines and one line belonging to the metal, λ 2852.

The sulphates of calcium, strontium, and barium give both bands of the oxides and lines of the elements. Phosphorus pentoxide yields a continuous spectrum with one peculiar line, seen also in the spectrum of arsenic.

The chlorides of the alkalies give also lines of the elements with a more or less continuous spectrum, which, it is believed, is due to the metal in each case. Lithium chloride gives no continuous spectrum.

The Volatility of Metals.—One of the most interesting facts ascertained by this investigation is the volatility of all the metals examined, except platinum, and particularly the extraordinary volatility of manganese, and, to some extent, of the infusible metal iridium. Metal believed to be pure iridium is seen to have diminished after the flame has played upon it for about two hours.

2. *New Calcium Lines.*—J. M. EDER and E. VALENTA state that they have discovered a new group of calcium lines in the ultra violet. These lines appear by the use of strong induction sparks and have the following wave lengths (i denotes relative brightness, for the strongest calcium line $i=10$, and for the weakest $i=1$):

	i		i
$\lambda = 2276{\cdot}0$	3	$\lambda = 2140{\cdot}3$	3
2259·5	1	2133·0	1
2208·3	4	2131·2	1
2200·5	1	2123·0	1
2197·6	3	2112·9	3
2170·0	1	2103·2	2
2152·3	1		

—*Wien. Anz.*, 1892, p. 252–253. J. T.

3. *The Hall Effect in Iron, Cobalt and Nickel.*—KUNDT has examined this effect in thin layers of the metals deposited by electrolysis on platinized glass, and states that in the three metals examined the Hall effect is proportional to the rotation of the plane of polarization of light in these metals in a magnetic field, and since the rotation of the plane of polarization in these metals is proportional to the magnetizing force, therefore the Hall effect is proportional to the magnetizing force. He states as a curious fact that electrolytically deposited bismuth shows a very weak Hall effect whereas cast bismuth shows the effect to a great degree.—*Ann. der Physik und Chemie*, no. 6, 1893, pp. 257–271. J. T.

4. *Measurement of Electrical Resistance by means of alternating Currents.*—F. KOHLRAUSCH in an important paper discusses the limits of the method which owes its elaboration to him. Other observers have criticized the method and the author takes up their criticism and discusses the results which have been obtained. He states that fluid resistances as high as 100,000 ohms can be measured with precision by his method. He shows how the introduction of condensers can in certain cases increase the accuracy of the measurements. The want of symmetry of the telephone which is employed on the Wheatstone Bridge is also discussed.—*Ann. der Physik und Chemie*, no. 6, 1893, pp. 225–256. J. T.

5. *A New Form of Induction Balance.*—The Hughes induction balance is an instrument of great sensitiveness, but it has not come into use in the measurement of specific resistance, for absolute measurements cannot be made with accuracy by means of it. It is true that Overbeck and Bergman have reached a fair degree of accuracy in the use of the balance, but the metals measured had

to be in the form of very thin plates. M. Wien shows how measurements can be made without resorting to a comparison with a standard metal—in other words, how absolute measurements can be made. In his method (1) one is independent of faults of contact and thermal effects at contact. (2) The measurement is made on metals in their natural state before they are influenced by wire drawing. (3) The specific resistance can be measured without determining a length.—*Ann. der Physik und Chemie*, no. 6, 1893, pp. 306–346. J. T.

6. *Specific Resistance of Mercury.*—J. V. JONES, adopting Lorenz's method of determining the ohm, has made a comparison of the ohm with the mercury unit and obtains the value

$$1 \text{ ohm} = 106{\cdot}307 \text{ mercury units.}$$

—*Phil. Trans. Roy. Soc. London*, 1891, vol. clxxxii, pp. 1–43. J. T.

7. *Photography of the Hertz Spark.*—EMDEN has examined the sparks produced by electrical resonance by means of a revolving mirror and photography and finds that they are oscillating sparks. —*Arch. d. Gen.* III, xxvi, p. 483, 1891. J. T.

8. *Green's use of "potential"*; by GEORGE F. BECKER. (Communicated.)—In the course of a paper* crediting D. Bernoulli with the introduction of the word potential into physics and arguing that Gauss's noun, the potential, was suggested by Bernoulli's term, I made the statement "Green did not use the *name* potential but only the adjective." I find that this statement requires a qualification. In his paper of 1828 on electricity and magnetism, the word potential occurs at least 125 times, and of these it appears as an adjective qualifying function in 124 cases. Once, however, in section 5, Green uses the phrase "the value of the potential for any point," thus printed both in the Crelle reprint and in Green's collected works. At first sight this seems a substantive use of the word, but I think this interpretation would be erroneous. Had he intended in this passage to introduce a new synonym for potential function, and to invent a noun not heretofore employed in any language, some explanatory phrase would almost certainly have indicated as much, and the use of the new term would surely have been repeated. There is no such phrase; and I have read the whole memoir twice through for the purpose of detecting a second case of the substantive use of potential, without success. Those who read Green's paper before the year 1840 can only have supposed that the phrase in section 5 was intended to be "the value of the potential *function* for any point"; for to such readers potential was known only as an adjective. It seems nearly certain, therefore, that either Green or his printer omitted the word function in this one instance by mere accident. Had Gauss never introduced the noun, no one, it seems to me, would ever have asserted on the strength of this passage that Green used potential as the name of function.

* This Journal, vol. xlv, p. 97, 1893.

9. *The Physical Review: A Journal of Experimental and Theoretical Physics*, conducted by EDWARD L. NICHOLS and ERNEST MERRITT. Vol. I, No. 1, pp. 1–80, July—August, 1893. (Published for Cornell University. Macmillan and Company, New York and London).—This new Journal gives the department of Physical Science what it has not had before in this country, a special periodical devoted to itself. The objects of the Physical Review, as given in the prospectus, are threefold: "To afford a channel for the publication of the results of research; to translate and reproduce in full, or in part, important foreign memoirs not easily accessible in the original to American readers; to discuss current topics of special interest to the student of Physics." It will be issued bi-monthly. The faithful carrying out of this program and the high standard of the Review in all parts is guaranteed by the able editorship of Professors Nichols and Merritt. It will doubtless receive from Physicist and the Scientific public in general the generous welcome which it deserves, and it should exert a powerful influence on the development of physical science in this country.

The opening number contains the following articles: The transmission spectra of certain substances in the infra-red by Ernest F. Nichols; relation between the lengths of the yard and the meter by W. A. Rogers; the infra-red spectra of the alkalies by Benjamin W. Snow (from Wiedemann's Annalen); the critical current density for copper deposition and the absolute velocity of migration of the copper ions by Samuel Sheldon and G. M. Downing; a geometrical proof of the three-ammeter method of measuring power by Frederick Bedell and Albert C. Crehore. The number closes with notes of scientific meetings and book notices. The mechanical execution of the work is all that could be desired.

10. *Polarization Rotatoire. Réflexion et Réfraction vitreuses; Réflexion Métallique.*—Leçons faites a la Sorbonne en 1891–1892, par G. FOUSSEREAU, rédigées par J. Lemoine. 343 pp. 8vo. Paris, 1893. (Georges Carré, Editeur).—This is an interesting and instructive volume discussing the whole subject of rotatory polarization. The method is simple and involves no excess of mathematical analysis. The four divisions under which the subject is treated, are: (1) natural rotatory polarization; (2) magnetic rotatory polarization; (3) vitreous reflection and refraction; (4) metallic reflection.

II. GEOLOGY AND NATURAL HISTORY.

1. *Lehrbuch der Petrographie von* F. ZIRKEL. Vol. I. Leipzig, 1893. 8vo. 845 pp. (Verlag von W. Engelmann).—Prof. Zirkel was not only one of the earliest petrographers, but was particularly the first of the European workers in this line who became well known to the American scientific public through his connection with the work of the survey of the 40th Parallel under

Mr. Clarence King. Therefore this work from his pen, in his chosen field after so long a silence—the reasons for which he states in the preface—will be without doubt eagerly welcomed and read by American petrographers and geologists.

The first volume, now issued, treats in the main of methods of petrographical research, the use of the microscope, of polarized light, of methods of separation and microchemical t[illegible] Then follows the microscopical physiography of the more important rock-making minerals, which are treated in detail only in respect to those points which are of immediate petrographical interest. The list of minerals thus made out has been somewhat arbitrarily selected—thus we note that vesuvianite, although common in contact metamorphic areas, is omitted, while dumortierite, for example, is given. No cuts of any kind are introduced, the author stating his reason in the preface for omitting them.

This portion of the subject occupies about half the volume, the remainder is taken up with general petrography—the various types of structures (comprising really texture as well) of rocks are then given, their general methods of geological form, of alterations by weathering, by contact metamorphism and dynamic forces, etc. Then the igneous rocks are taken up, and treated from a general standpoint, their chemical relations, processes of crystallization, differentiation of magmas, etc, ending with their classification. It would be impossible here to review this part of the work as it deserves:—suffice it to say that Prof. Zirkel divides the rocks for purposes of classification according to their mineral constitution, i. e., according to the feldspars or the lack of them, then according to structure which goes hand in hand with their geologic position, that is, plutonic or effusive. For the effusive (or porphyritic) rocks the distinction of geological age is retained, the rocks thus being divided into paleo- and neo-volcanic. Rosenbusch's family of the "dike rocks" is not recognized.

While it is probable that many petrographers will not agree with Prof. Zirkel on various points of theory and classification all will be thankful to him for the patient industry and rare discrimination with which he has brought together and digested such a vast amount of facts and material. These volumes when completed will form a work which no active investigator in this field can afford to do without. It is to be hoped the work will eventually be thoroughly indexed. L. V. P.

2. *Ueber das Norian oder Ober-Laurentian von Canada*, by F. D. Adams.—Of this memoir, in which Dr. Adams sums up the results of five years' work in the field supplemented by further study with the microscope and in the laboratory, it may be justly said that it is one of the most important contributions to the proper understanding of the Archæan in Canada that has yet been made. It is impossible to give here even a brief summary of the results attained. He proves that the so-called "anorthosite" rocks of Canada are of igneous character, that they have broken through the Laurentian and are in general massive in struc-

ture. In the neighborhood of the gneisses the rocks exhibit a peculiar cataclastic structure and are here only, gneissoid. They are shown to have an enormous geographical extension—in the Saguenay region the anorthosite extends over 5,000 square miles. It is concluded that these rocks were intruded around the shore lines of the ancient Archæan continent in pre-Cambrian times as modern volcanoes fringe the great oceanic areas.—*N. Jahrb. Min., B. B.*, viii, pp. 419–498. L. V. P.

3. *Brief notices of some recently described Minerals.*—SUNDTITE is a sulph-antimonate of silver and iron described by W. C. BRÖGGER from the silver mines of Oruro, Bolivia. It occurs in complex orthorhombic crystals and in massive forms. It shows no distinct cleavage, is very brittle and has a conchoidal fracture. Other characters are: hardness 3·4; specific gravity 5·50; luster metallic; color steel-gray. An analysis by G. Thesen gave

S	Sb	Ag	Cu	Fe
35·89	45·03	11·81	1·49	6·58=100·80

This leads to the formula $(Ag_2, Fe)S . Sb_2S_5$. The species is named after the mining director, L. Sundt.—*Zeitschr. Kryst.*, xxi, 193, 1893.

MARSHITE is native copper iodide described by C. W. Marsh from Broken Hill, New South Wales, and named after the describer by Prof. LIVERSIDGE. It occurs in very minute crystals implanted on a gossan-like siliceous cerussite. The crystals are referred to the hemihedral division of the tetragonal system. They are brittle; fracture subconchoidal; luster resinous; color reddish oil-brown; streak orange-yellow; transparent. The qualitative blowpipe and chemical characters fix the composition as iodide of copper, but a fuller examination of this and associated minerals is promised.—*Proc. Roy. Soc. N. S. W.*, xxvi, 326, 1892.

BURMITE is a new fossil resin from Upper Burma, described by Dr. Fritz Noetling in the Records of the Geological Survey of India, vol. xxvi, Part 1, 1893.

4. *Zoisite from the Flat Rock mine, Mitchell Co., North Carolina;* by W. E. HIDDEN. (Communicated.)—A pink, vitreous mineral, which I found entirely surrounding a large ovoid mass of very pure monazite, associated with a black, glassy allanite, has proved to be zoisite. The rare association made an analysis seem desirable, and this has been obtained through the kindness of Mr. L. G. Eakins of the U. S. Geological Survey. Mr. Eakins's analysis gave:

SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	H_2O
38·98	31·02	4·15	0·23	23·80	2·03 = 100·21

Sp. gravity 3·352 at 27° C. The water is strongly combined, not beginning to go off until a red heat is reached.

5. *Optical examination of Cacoxenite;* by LEA MCI. LUQUER. (Communicated).—The examination was made with a Beck lithological microscope, upon specimens from the following localities:

Trenic, Bohemia; Zbiroff, Bohemia; Weilburg, Baden; Zwickau, Saxony; Bearville, Lancaster Co., Penn., and Lobenstein, Russia. In general the crystals were exceedingly minute, and very much extended in the direction of one axis. The largest crystals noticed were from Lobenstein, but even these did not exceed $0{\cdot}04^{mm}$ in thickness. They all showed extinction parallel and at right angles to the long axis, and the larger crystals polarized in rather bright colors. The pleochroism was very slight, only being observed in the case of one or two of the largest crystals, when the color was an orange-yellow in the direction of the long axis and a light yellow at right angles to this axis. The average crystals from Zbiroff, were slightly larger than those from the other localities. In general the crystals appeared to be terminated by cleavage or pinacoidal planes at right angles to the long axis, although in some cases pencil-pointed terminations were noticed and also oblique and irregular terminations and fractures.

Two of the largest crystals from Lobenstein, showing terminations, were examined with the following results. In one case the terminations resembled pyramid or dome faces with the apex truncated by a pinacoid. Angle between pyramid or dome faces over the vertex $= 74° 20'$; angle (supplement) between these faces and the long sides of the crystal $= 37° 10'$. Angle between pinacoid and sides of crystal $= 90°$. In another case the terminations resembled pyramid or dome faces without any pinacoidal truncating plane. Angle between these faces over vertex $= 90°$ (approximately). These measured angles would give an axial ratio of $1 : \frac{3}{4}$. Some of the crystals also appeared to be modified in the direction of the long axis by prism or dome faces. The measurement of these angles was made on the revolving stage of the microscope, using the cross hairs in the eye-piece as reference lines, and the measured crystals were saved by cementing them to a glass slide with a very dilute solution of gum damar and benzole. Strengite, in very pretty pink botryoidal forms with drusy surface, was noticed occurring with the cacoxenite on limonite from Noble's mine, Bearville, Lancaster Co., Penn.

Mineralogical Laboratory, Columbia College.

6. *The Great Barrier Reef of Australia: its Products and Potentialities;* by W. SAVILLE KENT. With a chart, 48 photo-mezzotype plates, 16 chromo plates and many woodcuts. 380 pp. 4to. London, 1893 (W. H. Allen & Co.).—This beautiful and interesting volume presents the first results of the work accomplished by Mr. Saville Kent in his study of the Great Barrier Reef of Australia; a work which was made possible through the enlightened liberality of the Queensland Government. The more minute and technically scientific descriptions of the different forms of animal life, which the author has studied, are promised in a later publication. The work now completed presents, in a manner equally satisfactory to the scientific and to the general reader, a vivid picture of the marvellously varied and beautiful

life of a coral reef. It also gives an account of the economic importance of much of this life, and discusses in detail the observations which throw light upon the geological origin of coral reefs in general.

The region studied affords an unparalleld field for such an investigation. The Great Barrier Reef of Australia extends for a distance of 1250 miles along the coast of Queensland from Torres Straits to Lady Elliot Island, or from 9½° to 24° South Latitude. The outer edge of the reef is in some cases only 10 miles from the mainland while in others it is 150 miles and varying between these limits. A reef of such extent presents unique opportunities for the study of all the zoological and geological problems involved.

The attention of the reader is claimed first by the admirable portrayal and description of the beautiful life of the coral reef itself. Never before have those, who have known little of corals but the specimens mounted on the shelves of a museum, had such an opportunity to become acquainted with the living corals and the varied features of the growing reef. The author, skillful with his camera as with his pen, was able to secure many photographs not only of the scenes over the reefs in all their diversity of coral growths and groupings, but also of the expanded corals in their natural positions in the shallow waters. We cannot praise too highly the wonderful perfection with which the photographs are reproduced. To the senior editor they bring back vividly the delightful opportunities afforded him over fifty years ago, when in the U. S. Exploring Expedition under Commodore Wilkes, he studied corals and coral reefs in the Paumotus, Tahitian, Samoan and Fiji Islands. Other plates, not equal in execution to those just mentioned, give colored representations of the coral polyps, sea-anemones, etc. It would be difficult indeed to give any adequate idea of the variety of color displayed in the many kinds of animal life present in these coral gardens. The author's observations have resulted in adding many new genera and species to those previously recorded.

The formation of the Great Barrier Reef as a whole the author refers to a gradual subsidence, in accordance with the theory of Darwin.

In the chapter on the economical value of the living productions, it is stated that the reef-regions afford annually raw material for export to the value of £100,000. The pearl and pearl-shell fisheries are of prime importance, and so largely have the shells been gathered that an Act of Parliament has become necessary to prohibit their being taken in an immature state, that is, with a less diameter than six inches across the pearl lining. The author has succeeded in transplanting the young shells to quiet and shady waters where their growth was protected, and the artificial propagation thus shown to be possible may have important results. Another industry is that of collecting and curing the Bêche-de-mer, or sea-cucumber, used by the Chinese as an article

of food. It yields an average yearly revenue of £23,000. Another less valuable industry is that of the oyster which yields about £8000 annually. The food fishes also include a large number of recognized value, and others not yet utilized. The number of species of Queensland fish is stated to be nearly 900.

It is not possible to give an adequate impression of the wide general and scientific interest of Mr. Saville Kent's beautiful work. The geological student would derive from its illustrations an idea of the luxuriant growth of limestone-making seas that would be like a revelation to him; and to many the views would appear the more marvelous that all this growth is going on in shallow waters.

7. *Amount of water in the soil after a period of severe drought.*—M. Reiset (Comptes rendus, May 23, 1893) communicates some interesting facts relative to the effect of certain forms of vegetation upon very dry soil. The data are derived from observations made during the year 1887 when the rainfall was 5·87 meters instead of over 9·; the average. In June there fell only ·028 instead of ·073, and in July barely ·033 against the usual amount of 0·72. From the 4th of June to the 23d of July no rain fell. On the 2d of August, after a second period of drought, five samples of earth were taken from a depth of ·15 to ·25 below the surface, each containing from 8 to 10 kg. of soil, and each was quickly powdered, sifted to take out the pebbles, and placed in a glass-stoppered bottle. Two samples of 10 grams each were subjected to a temperature of 110° to 120° C. with the following results.

		Percentage of water.
1.	Under clover	4·84
2.	" wheat, about ripe	3·78
3	" scorched herbage	4·70
4.	" wheat in full growth	5·04
5.	" scorched lawn	7·84
6.	" wheat nearly ripe	3·81

Another observation eleven days later was made on the lawn-soil, no rain having fallen in the mean time. There was found a percentage of 6·80.

A second series of experiments was tried on soil, on the 9th of August, a good crop of wheat having been removed from it on the day before.

	Percentage of water.
Surface, at the roots of the wheat	1·22
At a depth of 0·20 slightly gravelly	4·95
" " 0·40 " "	9·47
" " 0·60 red clay	14·12
" " 0·80 "	21·81
" " 1·00 sub-soil red clay	26·18

Still another observation, on soil from which vetch and oats cultivated for fodder had been removed ten days before.

	Percentage of water.
At surface	1·30
" 0.20	6·03
" 0·40	7·87
" 0·60	11.42
" 0·80	12·45
" 1·00 subsoil	14·24

These tables are interpreted by M. Reiset as showing that while lawn-grass is wholly scorched in soil having 6·80 to 7·84 per cent of water, wheat can grow and ripen when there is only 1·22. The very vulnerable point in this conclusion is partially recognized by M. Reiset, who admits that at the time when his observations were made, the wheat was approaching or had reached maturity. Our readers can see that at that moment the wheat plant could get on fairly well with far less water than could the lawn-grass in the park. G. L. G.

8. *Nitrification.*—M. DEHÉRAIN (Comptes rendus, May 15, 1893) has recently reviewed this important subject, endeavoring to gain some hints as to the possibility of increasing the nitrificative activity of the soil in the spring. He was surprised at the prodigious amount of available nitrogen in soil received by him from diverse sources, and where there had probably been no addition of sodium nitrate as a manure. He at once began experiments on the effects of violent agitation on different soil, acting on a suggestion of Schlœsing that trituration and shaking by distributing the "ferments" might increase the energy. The soils on which he experimented were placed under different conditions: one sample of each being kept perfectly at rest; a second, exactly like the first, was from time to time for about six weeks stirred up very thoroughly and like the other exposed to the open air.

	Sample 1.		Sample 2.		Sample 3.	
	Kept still.	Shaken.	Kept still.	Shaken.	Kept still.	Shaken.
(1)	2	44	2	51	2	71
(2)	3	39	2	46	2	57

These figures are of milligrams of available nitrogen in 100 grams of soil.

Further interesting observations show that the ferments are not equally active at all times even in the same season, and further that the artificial increase in nitrificative activity at the beginning of winter when the useful products may be so easily lost is absolutely prejudicial.

Better appliances than those in use would appear to be demanded by the highest type of effective agriculture, and to this should be added also the selection of the most favorable time for stimulating such activity, namely just when the young plants are ready to utilize the products. G. L. G.

9. *The action of the Pyocyanic bacillus on plants.* — M. CHARRIN (Comptes rendus, May 8, 1893) presents an account of

his attempt to inoculate a thick leaved *Crassulacea* (Pachyphyton bracteosum) with one of the microbes which cause suppuration in animals. The effects depended largely on the amount of infecting material used; the characteristic tints did not appear where only a drop or two of the matter was employed; where more was taken the destruction of tissue was marked and the characteristic color was pronounced. There was a great accumulation of germs in the tissues, especially the intercellular spaces near the point of insertion, but the cells contained comparatively few. There were noticeable chemical changes in the tissues under observation, especially a diminution in the acidity of the foliar tissue, amounting sometimes to the ratio 225:120.

By this new and interesting chapter of comparative pathology it appears that in the vegetable as in the animal kingdom the activity of microbes (taken from the animal) depends on quantity as well as quality, and that these organisms utilize their secretions. They have the power of altering tissues, modifying their surroundings and changing the reaction of the liquids in which they act. In the two kingdoms there are many means of defence. In the vegetable world the principal one is the resistance offered by the cell wall to intracellular penetration, but in the plant there is no phagocytic defence. On the other hand the toxines are not effective to any great extent in the case of the plant, in fact this amounts almost to complete immunity. G. L. G.

III. Miscellaneous Scientific Intelligence.

1. *The John Strong Newberry Fund.*—The second joint meeting of the various scientific societies of New York City—the Scientific Alliance of New York—was held on March 27, 1893 and "had for its object the honoring of the name and fame of the late Prof. J. S. Newberry." The printed Proceedings of this meeting give the address of Prof. Fairchild, further a number of commemorative letters, a list of Prof. Newberry's scientific writings edited by Prof. Kemp, and finally the report of the Committee on the establishment of the John Strong Newberry Fund for Originial Scientific Research.

The plan, as accepted by the Council of the Scientific Alliance, contemplates the establishment of a fund of not less than $25,000, the income of which shall be devoted to the encouragement of scientific work in the departments with which Prof. Newberry was identified, viz: Geology, Paleontology, Zoology and Botany. Subscriptions large or small, are solicited and may be paid to the Secretary of the Committee, Prof. N. L. Britton.

2. *Cordoba Durchmusterung. Brightness and position of every fixed star down to the tenth magnitude comprised in the belt of the heavens between* 22 *and* 32 *degrees of south declination.* John M. Thome, Director. Buenos Aires, 1892.—This volume is the 16th of the Cordoba observations, and is the first part of a Durchmusterung Catalogue. It contains 179,800 stars, and is a

continuation southward of Argelander's and Schönfeld's work. It is to be followed by a second volume during this year, and an atlas of twelve plates. The two volumes and the atlas will cover the belt from 22° to 42° south declination, and will represent the result of 1,108,600 observations made by Mr. Thome and Mr. Tucker. The star-places are for the epoch 1875.0.

3. *Smithsonian Meteorological Tables* (based on Guyot's Meteorological and Physical Tables). 262 pp. 8vo. Washington, 1893.—(Smithsonian Miscellaneous Contributions, vol. xxxv, No. 884.) The fourth edition of Guyot's invaluable Tables was published in 1884 not long after the death of the lamented author; the completion of the work being performed by his assistant, Prof. Wm. Libbey. The present volume is one of three which, as stated by Professor Langley, are to supply the place of a fifth edition of these tables; the three parts into which the subject is to be divided being *Meteorological*, *Geographical* and *Physical*. Tables based upon the value of the meter provisionally assumed by the U. S. Coast and Geodetic Survey, (viz: 1 meter = 39·3700 inches, have been made by Mr. George E. Curtis. He has also prepared the entire manuscript and carried the work through the press, and to him therefore the many who will use it are deeply indebted. There are one hundred tables included, thermometrical, barometrical, hygrometrical, etc., and these are preceded by about fifty pages of text descriptive of their use.

4. *Forest Influences.* 197 pp. 8vo. Washington, 1893. (Bulletin, No. 7, U. S. Department of Agriculture, Forestry Division).—This is a timely presentation and discussion by B. E. Fernow and M. W. Harrington of the meteorological observations on record which bear upon the important influence of forest upon rainfall and climatic conditions in general. Appendices are added on the determination of the true amount of precipitation and its bearing on theories of forest influences by C. Abbe; also on the analysis of rainfall with relation to surface conditions by G. E. Curtis.

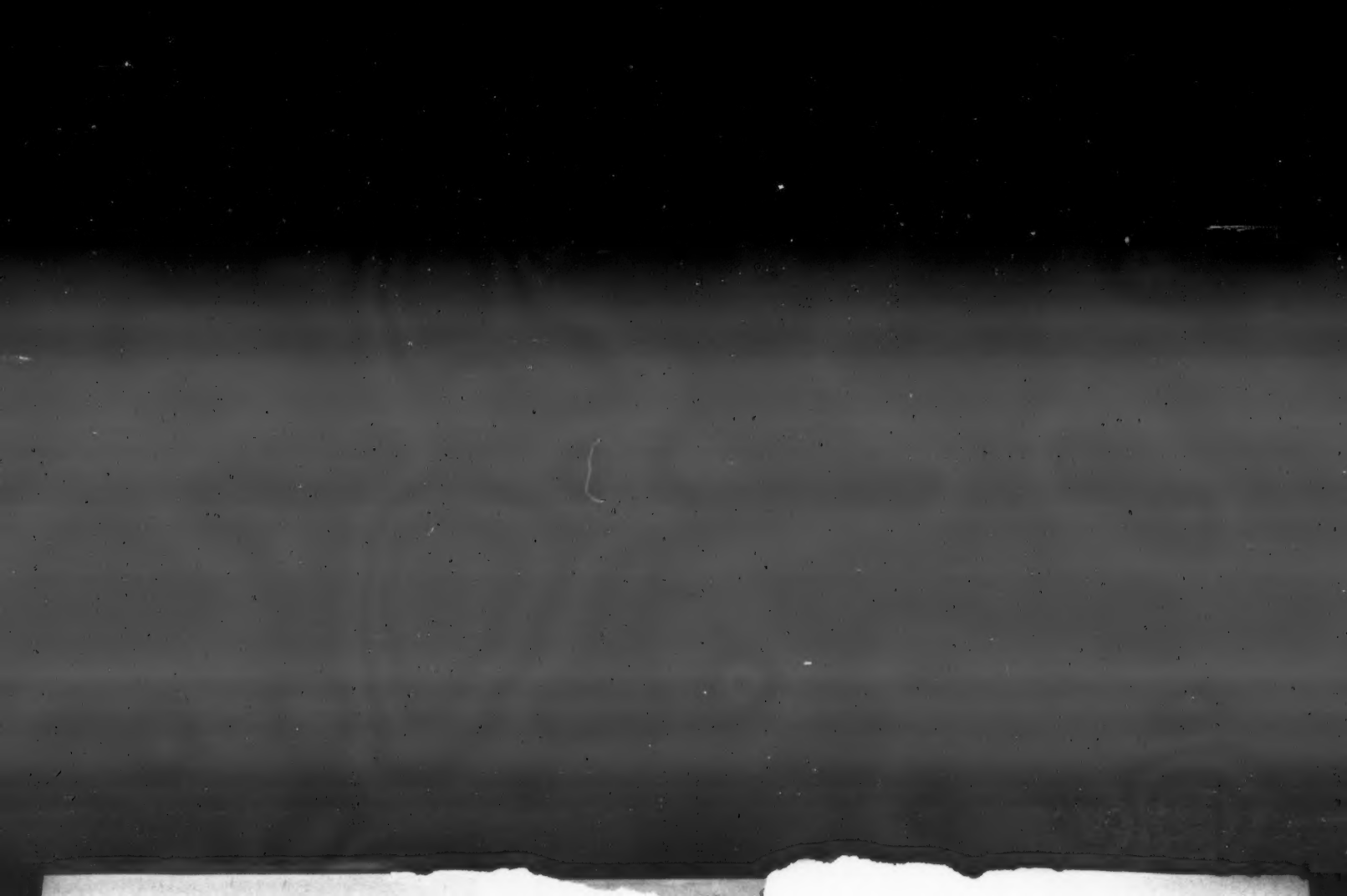
5. *Ostwald's Klassiker der exakten Wissenschaften Leipzig*, 1893. (Wilhelm Engelmann.)—The following are the titles of the volumes recently added to this valuable series:

No. 41. D. Joseph Gottlieb Kölreuter's vorläufige Nachricht von einigen das Geschlecht der Pflanzen betreffenden versuchen und Beobachtungen nebst Forsetzungen 1, 2 und 3 (1761–1766). 266 pp.

No. 42. Das Volumgesetz gasförmiger Verbindungen. Abhandlungen von Alex. v. Humboldt und J. F. Gay-Lussac (1805–1808). 42pp.

6. *Celestial Mechanics.*—The editors are informed that Dr. G. W. Hill will deliver a course of lectures on Celestial Mechanics at Columbia College, New York City, beginning about Oct 14th. One lecture will be given each week for thirty weeks. The course is free to all who desire to attend. Further information can be had on application to the department of Astronomy, Columbia College.

7. *Blaisdell's Physiologies.*—It is announced by Messrs. Ginn & Company, Boston, that they have purchased from Lee & Shepard Blaisdell's Series of Physiologies.



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